THE JOURNAL OF GENERAL CHEMISTRY OF THE USSR

Vol. 21 (1951)

No. 10 (October)

Publication of the Academy of Sciences of the USSR

IN ENGLISH TRANSLATION

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CONSULTANTS BUREAU

152 West 42nd Street
New York 18, N.Y.

Printed in Great Britain

Annual subscriptio $95.00
Single issue 12.00

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A. M. BUTLEROV

FOUNDER OF THE THEORY OF CHEMICAL STRUCTURE

(1861 - 1951)

S. N. Danilov

Organic chemistry was progressing very successfully in the 'sixties of the past century. It owed many of its outstanding achievements to the theory of the chemical structure of organic compounds, the author of which was Alexander Mikhailovich Butlerov (1828-1886), who set forth its major principles in his lecture at a scientific congress in Speyer, Germany, on September 19, 1861, and who substantiated it experimentally, together with his numerous disciples. Butlerov's structure theory and the periodic law of the chemical element [1], discovered in 1869 by another great compatriot of ours — Dmitri Ivanovich Mendeleev (1831-1907), underlie all the principal results of our study of matter; they imparted greater order and conclusiveness of content to chemical science, together with less planlessness in its future development. These major generalizations of modern science served to predict new chemical elements and interesting chemical and physical phenomena and resulted in the synthesis of a very large number of important and practically valuable substances.

Mendeleev's discovery of the periodic law and Butlerov's statement of the theory of chemical structure in chemistry are among the greatest historic events in natural science, outstanding successes of the materialist Weltanschauung and victories of dialectical materialism over agnosticism and idealism. The roots of these major scientific generalizations of modern chemistry and physics in our knowledge of matter go back to the even more general scientific and philosophical discoveries and inferences made by the Russian scientist of genius, Mikhail Vasilyevich Lomonosov (1711-1765), in the middle of the 18th century. Of the remarkable scientific creative power of M. V. Lomonosov, the following are appropriately listed here: the discovery of the natural law — the law of the conversation of matter and of the quantity of motion (the law of the conservation of energy) and, more particularly related to the periodic law of the chemical elements and the theory of chemical structure, his atomic-molecular doctrine (1738-1741), his interpretation of the concept of a chemical element, and his novel ideas on the relationship between molecular properties and the nature of their bonds and of the atoms constituting the molecule.

A disinterested survey of the historical development of theoretical concepts in organic chemistry must result in the firm conviction that the theory of the structure of organic chemicals should justly bear the name of Butlerov as its founder and architect.

In many of his theoretical papers and experimental researches A. M. Butlerov expounded the structure theory and fought for its recognition and correct understanding in Russia and abroad.

Guided by the structure theory, he predicted new chemical compounds and previously unknown chemical transformations and realized them experimentally.

The views Butlerov had elaborated concerning the chemical structure of substances, the meaning of a chemical formula, the inadequacy of Gerhardt's theory of unitary types then dominant in the science, and the incorrectness of some conclusions of Gerhardt's and other chemists (Kolbe, Kekulé, and Wurtz) were already being used in lectures on organic chemistry and in scientific research at the University of Kazan in the late fifties and the early sixties [4].

Somewhat earlier, in 1858, Butlerov read his first theoretical paper on an article by Cowper, "A New Chemical Theory", asserting that 'the time has come to go beyond Gerhardt'.

His report read at the meeting of the chemical section of the Congress of Physicians and Natural Philosophers in Speyer in 1861, entitled "The Chemical Structure of Matter", not only contains "a summary of the ideas underlying the generally adopted theoretical concepts, together with an expression of these ideas freed from everything erroneous", as Butlerov stated [3], but also a fundamentally new posing of the problem of the chemical nature of compounds and the significance of chemical formulas.

A. M. Butlerov's notable book [5] "Introduction to the special study of organic chemistry", written in Kazan in 1863-1864, renders great services in disseminating the structure theory among chemists at home and abroad during the sixties.

In this book the structure theory was systematically applied to a study of various groups and examples of organic substances; it sets forth fundamental concepts including that concerning the chemical structure of compounds and a clear outline of the evolution of theoretical concepts in chemistry.

Butlerov repeatedly pointed out the close link between the theory of chemical structure and preceding theories in organic chemistry.

The following scientists played a prominent part in the evolution of theoretical concepts in chemistry during the first half of the nineteenth century: J. J. Berzelius (1779-1848) – the theory of radicals and the electrochemical theory; J. von Liebig (1803-1873) – the theory of radicals and the theory of polybasic acids; J. B. A. Dumas (1800-1884) – the etherin theory and the theory of radicals and types; A. W. H. Kolbe (1818-1884) – the theory of radicals, combined with the substitution theory); A. Laurent (1807-1851) – the substitution theory and the nucleus theory; C. F. Gerhardt (1816-1856) – the unitary system, the law of residues; and others.

During the forties and fifties it was the unitary theory that found widest acceptance, as a continuation of the theory of radicals, the theory of radicals, the substitution theory, and the doctrine of homologous series (Schill, 1842). Earlier (1848) in a textbook of his, Gerhardt had preferred empirical formulas, but at a later date (1853-1856) he introduced "type" formulas in his Manual of organic chemistry.

Chemical (rational) formulas, he believed, could represent relationships, analogies, and reactions, but not the arrangement of the atoms within a molecule (constitution), however. Gerhardt's great mistake – the consequence of his agnosticism and not merely of the prevailing level of knowledge at the time – was his conviction that all that a chemist could learn from a study of chemical reactions was the past and the future of a substance, and not its present state,

i.e., not the constitution of a molecule. Gerhardt admitted various formulas for a single substance, depending upon the reactions from whose study the typical formula had been derived.

Our chemists, especially Butlerov, took a critical view of Gerhardt's unitary system (theory). Even before Butlerov, Russian chemists had made their own, though small, contribution to the evolution of theoretical notions in organic chemistry.

N. N Beketov (1826-1911), a pupil of the famous N. N. Zinin (1812-1880) and later an academician, had reached valuable theoretical conclusions in his dissertation, completed in Zinin's laboratory in the Academy of Medicine and Surgery, and in other researches of his. In 1853, Beketov wrote [7] as follows concerning Gerhardt's views on the substitution of residues in nitrobenzoic acids: "It seems to me that the contradiction in the theory of the French chemist is solely due to the fact that his attention was concentrated on a single symmetry in the reactions, while their chemical meaning, which depends upon the values of the elements taking part, was ignored by him". According to Beketov, the properties of every atom in a molecule depend upon the other atoms in the molecule. His reasoning is directly related to the idea of mutual influences between the atoms in a molecule, clearly expressed in Butlerov's papers and subsequently elaborated by V. V. Markovnikov (1838-1904) [8].

We find N.N. Sokolov (1826-1877) discussing Gerhardt's views; he finds it impossible to accept Gerhardt's types as something unchangeable or that a given compound cannot belong to various types no matter what the conditions to which the compound is subjected. In some of his papers [9] Sokolov discusses the problem of the effect of the external medium upon the properties of compounds, the Gerhardt type theory, and the properties of hydrogen in various molecules. It is worthy of note that Sokolov's views aided him to clear up the basicity and tomicity of lactic acid. Butlerov attached [4] some importance to these assertions of Sokolov's, which resembled his own, but dealt with a special case, whereas the structure theory formulated these problems more correctly and in a more universal manner.

By 1861 correct atomic weights had gradually been added to the science, as well as accurate notions of the equivalent, the atom, the molecule, and the atomicity (basicity, valence) of elements and carbon residues (Gerhardt, Laurent, Cannizzaro, Frankland, Odling, and others). A. W. H. Kolbe and later more especially A. Kekulé pointed out (1857) the tetra-atomicity (tetravalence) of carbon [10].

The doctrine of the atomicity of atoms and radicals gave rise to the conception of limits in the composition of mineral and organic acids. D. I. Mendeleev, who worked in organic chemistry during the initial years of his scientific career [11], published "An essay on the theory of limits of organic compounds" in 1861. Frankland and, more particularly, Cahours had previously spoken of the limits in the composition of metallic and organometallic compounds.

According to Mendeleev, addition reactions, rather than substitution ones, are typical of unsaturated hydrocarbons, the saturated $C_n H_{2n+2}$ series being the limit of the unsaturated hydrocarbon series.

Butlerov stressed the great importance of the notion of the atomicity of atoms and of groups of atoms in elaborating the theory of the chemical structure of organic compounds [5]. As he saw it, the idea that carbon atoms may be linked together and other atoms may be added, depending upon the atom valency and with limits fixed by the constitution of carbon compounds, was of great aid in the writing of formulas and the derivation of possible isomers.

The notions of the interlinking of atoms was expressed more clearly by Kekulé and especially by Couper at the very end of the fifties.

The conclusions that carbon atoms were tetravalent and that they were linked together and to other elements, which are the particular achievements of Couper and Kekulé, may be termed the law of the linkage of atoms in molecules of organic substances. Although the rules on atomic valency and bonds, subsequently brought to a high stage of refinement (the number of isomers, multiple bonds, rings, etc.), with Butlerov playing a major part in this development, are employed in the writing of contemporary structural formulas, it would be incorrect to liken these rules to Butlerov's theory of chemical structure, setting them up as equals, as Lother Meyer apparently did [12] (1868), failing to comprehend the essence of the theory of chemical structure and wrongly denying Butlerov's merits. It is understood that the structure theory comprised all that was valuable, corresponding to experimental data, in the radical theory, the substitution theory, the theory of homologs, and the like.

Neither Kekulé not Cowper included chemical content in the rule of atomic linkage, regarding it as formal and external. In his papers and in his textbook Kekulé confined himself to general considerations, which he himself deprecated. Cowper considered the formulas outwardly, without furnishing proof of their correctness or making any inferences about isomerism.

It was Butlerov who defended the idea of chemical structure and of a single formula for each compound, reaching profound conclusions, predicting possible isomers, and synthesizing many of these isomers.

Cowper claimed the authorship of the idea of the linkage of atoms in molecules on the basis of the fixed valency of the elements, though many sources in the literature point out Kekulé's priority.

For some years after Butlerov had put forward the structure theory, Kekulé continued to support Gerhardt's theory of types, and though recognizing its limitations, he did not see any practical significance in the rules of atomic linkage [13].

Kekulé's paper (1858) "On the constitution and metamorphoses of chemical compounds and the chemical nature of carbon" [14] describes how carbon atoms are kept together and how they keep other atoms by virtue of this property. He puts forward the interesting idea that it is not the major task of a chemist to discover the atom groups within a molecule, as the radical theory had assumed, nor in classifying compounds according to a few types, which he regarded as merely model formulas, but to ascertain the constitution of radicals and their nature from the known nature of the elements. This objective closely resembles those posed by Butlerov in his 1861 lecture, which he solved.

But in his conclusion Kekulé stated that considerations of this nature are of merely subordinate importance. In his comprehensive textbook of organic chemistry [15] he made the same remarks, but in practice he found the use of type formulas more convenient. He supplemented Gerhardt's types by introducing the methane type (tetravalent carbon). Kekulé denoted atoms by interlinked circles only to demonstrate a method of representing the formulas.

Cowper went much farther than Kekulé in his demonstration and use of the atom-linkage rules [16]. His single paper, however, contains no chemical proofs of the written formulas, which resulted in the errors noted by Butlerov in his Paris lecture and paper (1858) on the occasion of Cowper's remarks. Although Butlerov pointed out serious misunderstandings in Cowper's paper, in his later articles he speaks [12] of the resemblance between the Cowper formulas and the

chemical formulas of the structure theory and their fundamental differences from the type formulas of Kekulé.

Wurtz (1817-1884) found (in 1858) that Cowper's formulas were too arbitrary and, as a supporter of the type and substitution theory, wrote: "we do not claim to represent the internal constitution of compounds by means of our rational formulas. All that these formulas need do is represent the reactions that are accessible to experiment and demonstrated by the latter. Therein lies their advantage". These words of Wurtz [17] reflect an excessive overestimate of the demonstrability of type formulas. Wurtz approved Kekulé's words of mistrust, referred to above, in his own assertions regarding the feasibility of representation by formulas based on the idea of atomic linkage and the fact that Kekulé actually preferred type formulas. It may be noted, in passing, that Kolbe, in contrast to Gerhardt and Wurtz, acknowledged only a single formula for any one compound. Remaining an adherent [18] of the radical and substitution theory for many years, Kolbe did not welcome Butlerov's ideas of chemical structure any more than he did the stereochemical theory of van't Hoff and Le Bel somewhat later. Although notions of constitution and of the points of application of chemical affinity and atomicity slipped into Kolbe's utterances, he clung to the opinion that "we shall never be able to obtain, from our researches, a clear idea of how the individual atoms are arranged with respect to one another". Science has disproved the agnostic views of Gerhardt, Kolbe, and other scientists. Butlerov endeavored to find in Kolbe's papers traces of a resemblance to his assertions concerning chemical structure, but Kolbe opposed the theory of chemical structure for several years: "I cannot get any idea of the manner in which the elementary atoms are related together within a molecule".

Though the supporters of the radical theory and of the type and substitution theory had talked about the constitution of matter for years, this concept had a different content for the various authors. The supporters of Berzelius asserted that their rational (so-called in contrast to elementary) formulas expressed the chemical constitution of matter as a sort of pre-existence, an occurrence of simpler substances. Gerhardt used the term 'molecular constitution' for the arrangement of atoms, but he denied it was possible to judge of this arrangement from chemical phenomena, such as various examples of the formation of substances. The followers of Gerhardt, even Kekulé, believed that knowledge of the internal structure of a compound (its real structure) could be secured more readily by physical research. The 'typists' understood the term 'constitution' to mean actually the spatial arrangement of atoms. According to Kolbe, chemical constitution signified the chemical interrelationships between the various equivalents, but not their arrangement in space. It would seem that he was approaching the position held by Butlerov. Kolbe expressed his views on this question not too clearly, but he did acknowledge that there must be a single rational formula for a substance. Laurent [19] likewise insisted that an idea of the constitution of a compound (the prearrangement of the atoms) could be gathered from the chemical properties of substances.

Kolbe employed the substitution principle, at times to the prejudice of the issue, being absorbed, as Butlerov put it [20], by the outward appearance of the formulas and forgetting the constitution of matter. His substitution formulas were not always borne out by the facts. But since the substitution principle was fundamentally correct, it is not surprising that Kolbe foretold the possible existence of tertiary alcohols, though this postulate regarding the existence of tertiary alcohols followed much more definitely from Butlerov's theory of chemical structure. Butlerov and his pupil (A. N. Popov) corrected

Kolbe's false conslusions concerning isomeric ketones, as well as Kekulé's conclusion (1865) that there are three alcohols related to propane, instead of only two isomers. Kekulé, who took the term 'constitution' to mean the arrangement of atoms in space and held on to the notion of rational formulas as transformation and analogy formulas, assumed that a single substance could have several formulas. Rejecting expanded rational formulas and preferring type formulas, he differed with Butlerov in doubting that it was possible to express the spatial arrangement of atoms by means of formulas.

After Butlerov's lecture at Speyer, Kekulé announced that he was abandoning type formulas and rational formulas in general and would henceforth use nothing but empirical formulas, while refusing to support Butlerov's new views.

In his textbook [15], Kekulé expresses a relativistic attitude toward theories, asserting that there could be no thought of a real theory in chemistry as long as theoretical views were based upon probabilities and expediency, so that different chemists might hold differing views.

Butlerov set forth the essential features of his views in brief though significant words in his Speyer (1861) report [21] on the chemical structure of substances, views that were perfected in his later works.

He bagan his historic lecture by pointing out that the theoretical side of chemistry was out of step with its factual development. In his brief but clear critical survey of the state of theoretical concepts in the chemistry of the time, the lecturer commented on the inadequacy of the type theory, the futility of complex types, the total inadmissibility of having many rational formulas (in Gerhardt's use of the term) for a single substance.

Of the many faults of the type formulas, Butlerov regarded as most serious the fact that type formulas did not express addition reactions, as in the case of ethylene.

He pointed out the significance of the fact that Dumas' idea of mechanical (carbon) types, the respective hydrocarbon being taken as the compound type, had given rise to the notion of the atomicity of elements and of the consequent atomicity of groups. "The time has come", Butlerov asserted, "for Gerhardt's theory to yield to the concept of the atomicity of equivalents".

In his report he rejected the incorrect view held by Gerhardt and his followers that it was impossible to infer the position of the atoms within a molecule from the latter's chemical transformations, though Laurent had already demonstrated that "inferences about this structure are not entirely beyond our reach".

A profound thought is expressed in Butlerov's words: "the chemical properties of a complex substance are due principally to the chemical relationships of the elements that go to make it up". He put aside for the moment the problem of the spatial arrangement of atoms in molecules (the constitution of compounds, according to the views of Gerhardt's supporters). A new and fruitful concept of chemical structure was the central feature of the report: "I define chemical structure as the distribution of the action of this force (chemical force, affinity), as a result of which the chemical atoms are combined into a chemical molecule, influencing one another directly or indirectly". The same thought is conveyed in the German translation of the report: "I would call chemical structure a chemical bond or the way in which atoms are combined together in a complex body".

A quite clear answer is given to the question of what affects the properties of chemical compounds: " The chemical nature of a complex molecule is governed by the nature of its constituent elementary parts, their number, and their chemical structure." Further research should shed more light on " how much the chemical properties of a substance depend upon chemical structure."

Contradicting the " typists," Butlerov asserted that " the present state of our knowledge proves the feasibility of determining chemical structure." The link between the new concepts and the old was demonstrated, using the amine group as an example: " Speaking of the chemical constitution of these substances, we find ourselves involuntarily considering not merely their types and the atomicity of their elementary constituents, but also the way in which these latter interact chemically." The structure of substances is established by studying methods of synthetic formation and, indirectly, by analytical reactions (cleavage reactions). Double decomposition (exchange) reactions are likewise of importance in establishing structure. The report thus furnishes clear indications of how the chemical structure of organic compounds should be established.

The brief, significant definitions of the concept of chemical structure are repeated in the Introduction to the special study of organic chemistry. There Butlerov explains what chemical formulas should be called rational ones: " In the interaction of various equivalents, radicals and residues, we have to consider the order of chemical interaction (or the order of the mutual chemical bond) between various elementary equivalents, the result of which will be the existence of a given molecule. This order of interaction - the way in which the elementary equivalents are bound together chemically within the molecule - may be termed the chemical structure of molecules, and, at the present state of the science, it would be correct to call only those formulas that express the chemical structure of molecules 'rational formulas.' " The term " equivalents" signifies chemical atoms.

Returning to the Speyer lecture, we must mention that the lecture discussed 8 rules nearly all of which underlie the formulas of Butlerov's theory of chemical structure and may add in the recognition of chemical structure:

1) The concept of mono-, di-. triatomic, etc., equivalents and of the presence of a definite amount of the force (affinity) producing chemical phenomena in every elementary equivalent.

2) A distinction between the concept of the amount of affinity and that of its intensity, the amount of energy by which substances are connected together, " this intensity varies, depending on the nature of the reacting substances and on the conditions in which the action occurs," differences in the unities of affinity being of no importance for isomerism.

3)-7) The odd or even number of affinities when equivalents react; the even number of units of a free affinity; the expression of the aggregate affinities (a minimum of two) by even numbers for a chemical reaction between atoms; the direct combination of substances, provided they possess an even number of affinities; the combination of elementary polyatomic equivalents within complex substances with identical equivalents having free affinities, which is responsible for the accumulation of unlimited quantities of such equivalents within molecules, and so forth.

8) The ability of a complex substance to combine directly with various molecules via the element all of whose affinity has not been used up in the formation of the complex substance; otherwise the substance can only enter into double decomposition reactions.

Butlerov concludes that the doctrine of types is of secondary importance for organic chemistry and that the chemical structure, dependent upon an element's atomicity, must be considered. At the same time he takes note of the difficulties involved in determining the atomicity of some substances and in explaining why some substances, the existence of which is possible theoretically, actually do not appear to exist (the failure to synthesize methylene, etc.).

Butlerov's conception of a chemical formula attracts attention: " If we now endeavor to define the chemical structure of substances and we succeed in expressing it by our formulas, these formulas will be, even if only partially, still to a certain degree real rational formulas. In this sense there will be one possible rational formula for every substance, and when the general laws governing the chemical properties of substances as functions of their chemical structure have been discovered, such a formula will express all these properties." As for type formulas, in their present form their use should be discontinued. Butlerov stated: " Time and experiment will best of all show what the formulas of chemical structure will look like."

He concluded his report with the following words: " It is time to base our concepts of the chemical constitution of substances upon their atomicity and chemical structure, discarding type notions entirely."

The 1861 Speyer report was soon followed by a series of Butlerov's trailblazing theoretical papers and experimental researches. The establishment of possible isomers in the saturated and ethylenic hydrocarbons and their discovery by Butlerov and his pupils incontrovertibly played a major part in the development and recognition of the structure theory.

At the beginning of the sixties the problem of isomerism was in a confused state. There were no definite data on isomerism even for the first few representatives of the paraffin and ethylene hydrocarbons. Two formulas were employed for ethane, for instance, it being regarded as ethyl hydride and as dimethyl. The known isomeric substances in the sixties and seventies comprised those that were later correctly considered to be structural isomers in accordance with structure theory, and another, rather extensive group of physical isomers, including the optical and geometrical steric isomers. Butlerov outlined the distinction between chemical and physical isomerism, and turned to a study of chemical isomerism [22]. His work on isomerism was crowned with remarkable success.

His unerring prediction of isomers of the members of homologous series, followed by their synthesis in exactly the number predicted by theory, was a direct proof of the fruitfulness and correctness of the theory of chemical structure. And even today, notwithstanding the well-known and customary major successes of synthetic organic chemistry, it is still astonishing that the theory enables us to foresee the existence and the methods of synthesis of isomers and many other substances of the most complicated and, one might say, fantastic structure.

Butlerov's comprehensive paper, " On various ways of explaining some instances of isomerism," appeared in 1863 [23]. This paper was soon followed (1864) by others: " The systematic use of the atomicity principle in forecasting instances of isomery and metamery" [24]; and " A synthetic method of producing alcohols and the chemical structure of ethylene" [25]; and " The chemical structure of some unsaturated hydrocarbons" [26]. All of these theoretical and experimental researches of Butlerov, in addition to other papers of his, extended and corroborated the structure theory. During these same years V. V. Markovnikov, a pupil of Butlerov's, also published interesting material on isomerism (1864). His master's thesis [27] and his papers contained much valuable experimental data and many theoretical infer-

ences (1865).

Butlerov's 1863 paper contains a comprehensive critical review of the contemporary state of theoretical concepts (Kolbe, Kekulé, Gerhardt, and Wurtz), which had been dealt with briefly in his 1861 report, and gives examples of isomers, besides discussing the effect of chemical structure upon isomerism.

Whereas Butlerov considered the phenomena of isomerism to be highly significant, Kekulé said relatively little about it in his papers or in his textbook, which is the subject of comment by Butlerov. He had to reject some of Kekule's and Kolbe's formulas as contradicting the rule of atomicity and the theory of chemical structure. He gives a highly profound explanation of the problem of mutual atomic influences upon the chemical structure of a substance, which is of interest today in connection with electronic concepts of these effects, which have been evolved on the basis of Butlerov s and Markovnikov's doctrine of mutual interactions between atoms, which is an inseparable part of the theory of chemical structure. He advances the hypothesis that " even atoms that are less directly linked to other atoms may still affect chemical nature" and that " the number of atoms is of much more limited significance than their nature upon the chemical character of the atoms and groups linked to them."

The problem of the structure of ethylene hydrocarbons and other ethylene compounds is posed in the same manner. A symmetrical arrangement of the hydrogen atoms about the carbon atoms is given for ethylene.

In correcting the formulas given by Kolbe and Kekulé for some substances, Butlerov states that " the criterion of chemical structure is much more useful in searching along correct lines for the causes of isomery than schematic derivation of a formula by way of substitution."

The formation of ethylene hydrocarbons is depicted as the result of the union of many molecules of the hypothetical methylene, while the structure of Wurtz's polyethylene glycols and amino alcohols and the corresponding " diglycol acids" are discussed. The existence of isomeric aminated polyglycolic acids, subsequently synthesized by Heintz, is predicted [24].

In this paper the bonds between atoms are represented by parentheses, and the old notation for equivalents is used, so that the external appearance of the formulas as written resembles that of the type formulas, although differing from the latter essentially. Butlerov therefore expected that they would be more readily understood by his contemporaries.

This meaty paper concludes with the words " May the viewpoint expressed above stimulate experiment along these lines."

The paper [28] entitled " A tertiary pseudo-butyl alcohol (trimethylated methyl alcohol" is highly valuable both experimentally and theoretically. Describing his famous synthesis of trimethylcarbinol, the existence of which had been predicted by Kolbe on the basis of the substitution method and by Butlerov himself as a corollary of the structure theory, Butlerov arrives at general inferences regarding the existence of isomerism Prior to that all sorts of views had been current about the reasons for isomerism, but all of these reasons could be reduced to a difference in chemical structure.

" As I see it, this difference involves a dissimilar distribution of the chemical action of the affinity units of the atoms in question, Butlerov writes.

Resolving the ethylene problem in favor of the symmetrical arrangement of the hydrogen atoms, he regards Erlenmeyer's opinion that a difference in the distrib-

ution of the hydrogen atoms about the two carbon atoms (in ethylene and ethylidene) could not explain the difference in their properties, alleging that this difference was due to a difference in the equivalents (affinity units) of the polygenic (polyatomic) carbon atom, as unfounded. For some time Erlenmeyer [19] endeavored to prove that isomerism based upon an unequal number of affinity units, in other words, a difference in the comparative magnitude of the affinity, could also exist in other cases. Prior to that, Butlerov had thought such a hypothesis possible, but he later found it unnecessary [21,23] in establishing isomerism.

Certain considerations led Kekulé [30] to an erroneous view of the existence of three propyl alcohols, allegedly on the basis of the atomicity theory (1865,1866).

The only inescapable conclusion, according to Butlerov, was that " the way in which one part of the affinity of a polygenic atom was attached affects not only the relative magnitude of the other part of the affinity, but also the chemical nature of the atoms or groups linked by this affinity." This is another instance, we see, of the idea of the mutual influences between atoms within a molecule expressed previously.

Butlerov considered that a study of the isomerism of alcohols might yield valuable insight into the causes of isomerism in general, and this was brilliantly confirmed in the case of trimethylcarbinol and other alcohols (the 1864 proof of the existence of eight isomers [28] of amyl alcohol). It was also pointed out that only one isomer of ethane can exist, as followed from the new data provided in 1864 by Schorlemmer, who demonstrated the error in Frankland's conclusion (in 1851) that the hydrocarbon C_2H_8 had two isomers.

In another paper that also dealt with tertiary alcohols [31], Butlerov used the experiments of A. N. Popov [32] in Butlerov's laboratory in 1864 to demonstrate Kolbe's mistake in connection with the isomerism of the ketones.

Butlerov's paper in which he described [24] the systematic application of the atomicity principle to the forecasting of instances of isomerism and metamerism was widely used in textbooks of organic chemistry, in the chapters describing isomerism in various homologous series. Once this paper had been published, the inferring and forecasting of instances of isomerism and metamerism became a purely routine task.

He also commented on the importance of knowing which of the compounds that might possibly exist according to the principles of atomicity and chemical structure actually did exist.

Butlerov continued to predict instances of isomerism and metamerism in various papers. Of considerable interest in this connection is the 1867 paper " On derivatives of trimethycarbinol (a tertiary butyl pseudoalcohol)." Here [33] he explains the isomerism of butane (C_4H_{10}) and of butylene (C_4H_8). Thus the theory was borne out by experiment.

Butane, or diethyl, had been known previously (Frankland and Cheyenne), while Butlerov had secured isobutane (trimethylformene) from trimethylcarbinol and compared its properties with those of butane. This was the first instance in which a hydrocarbon isomerism that had been predicted by the structure theory was subsequently discovered. Earlier (1864) isobutylene had been synthesized in the Kazan laboratory; now it was described in detail. It was found to differ from the butylenes synthesized previously: Faraday's ditetryl (1825) i.e. Butene-1; and de Lunin's butylene (1864), i.e. butene-2. Butlerov derived the three isomers of the hydrocarbon C_4H_8 and established the structure of isobutylene.

Butlerov's conclusions at the end of his paper indicated his absolute convic-

tion that the structure theory was " the best guide in the investigation of the problems of isomerism."

In his subsequent researches Butlerov made a study of the principal transformations of ethylene hydrocarbons and dealt with the problem of their structure. The problem of the isomerism of ethylene hydrocarbons and of how to write their formulas with a double bond was handled in its final form in the 1870 [35] paper entitled " The chemical structure of some unsaturated hydrocarbons." Butlerov's words: " Unsaturated carbon compounds (with the exception of carbon monoxide) have no free affinities in the full sense of the word at all, though certain carbon equivalents are linked together doubly or triply in them," must be regarded as a substantial step forward in the structure theory.

The unerring prediction of isomers of members of homologous series and their experimental production in exactly the quantities prescribed by the theory, the arranging of all the wealth of organic chemistry in an orderly system, with a single formula assigned to every substance, the discovery on the basis of this theory, of new compounds and even of new groups of substances, and the successful multistage syntheses following a definite plan - all these soon convinced chemists of the correctness and fruitfulness of the structure theory. The most striking theoretical inferences and many remarkable practical discoveries that established the fame of the structure theory were achieved by Butlerov and his celebrated school.

After Butlerov's papers had been published in the sixties, most chemists gradually began to employ the structure theory in their own research. There is no longer any room for doubt that Kekulé actually continued to use type formulas for several years even after 1861, manifesting considerable inconsistency in his statements and in his choice of formulas for organic compounds and in his manner of representing them, remaining a " typist" for several years. A comparison of the historical data makes the reproofs addressed to Kekulé by V. V. Markovnikov and other chemists (including some abroad) as far back as the sixties, for permitting contradictions to creep into his papers indicates that they were entirely justified. Giving Kekulé all due credit for his great contributions to the development of various branches of organic chemistry, and appreciating the part he played in the evolution of theoretical concepts, particularly in the fifties, and his brilliant solution of the problem of the structure of aromatic compounds (though not without being influenced by Cowper's and Loschmidt's formulas and, especially, by the achievements of the structure theory), there is no reason, however, to credit him with the leading role in the elaboration and introduction into science of the theory of chemical structure, which is Butlerov's achievement.

The benzene theory (1855) really was a great scientific achievement, elucidating the complicated and manifold group of aromatic substances The German scientist A. von Baeyer [36] expressed the significance of these researches of Kekulé in the following words: " If we were to compare structural chemistry to a house, then the benzene theory would be the capstone." But the very edifice of the structural theory was built by A. M. Butlerov.

The astonishing fertility and clarity of the basic principles of Butlerov's theory of the structure of chemical compounds are the reasons for its fairly rapid acceptance (though not at once) by chemists both at home and abroad, who began to employ it in their research as a truly scientific chemical theory.

It was only after the development of the structure theory on the basis of Butlerov's clear formulation of the problem of the chemical structure of the molecule and the spatial arrangement of atoms within it that van't Hoff (in 1874)

used the tetrahedral model of the carbon atom, first suggested by Butlerov in 1862 [13] to supply a definite criterion - the asymmetric carbon atom - for distinguishing molecular asymmetry, which was the cause of optical activity according to L. Pasteur. The theory of geometrical isomerism also grew out of the concept of the tetrahedral configuration of the carbon atom.

The reasons for the existence of the large group of physical isomers were cleared up; Butlerov had turned away from a detailed study of this group in the sixtues, setting as his objective the elucidation of the chemical structure of molecules.

But even after stereochemistry had brilliantly corroborated the predictions of the chemical theory of molecular structure Butlerov continued to expound the structure theory, fighting for it even within the walls of the University of St. Petersburg (now the A. A. Zhdanov University of Leningrad), where he held a professorship.

In reply to articles published in 1879 and 1884 by a professor of the university, the eminent chemist N. A. Menshutkin (1842-1907), attacking the structure theory and defending the long-establised substitution theory [37], A. M. Butlerov delivered lectures and wrote articles (in 1879 and 1885) by way of explanation and rejoinder.

In 1879 he delivered a very lively lecture [38] at a meeting of the Russian Physical Chemical Society entitled: " The present significance of the theory of chemical structure."

His 1885 paper: " Chemical structure and the substitution theory," distinguished by a wealth of very profound ideas, indicates that Butlerov took a firm materialist position at the end as well as at the beginning of his scientific career [39].

For a quarter of a century A. M Butlerov carefully hammered out the theory of chemical structure, proving himself to be an outstanding theoretician and a skilful experimenter.

A portrait of the eminent scientist is conveyed in the words used by D. I. Mendeleev in 1868 in his testimonial to Butlerov's researches [40]: " With Butlerov all his discoveries stemmed from and were guided by one general idea. This idea has founded a school, and this idea enables us to say that his name will forever remain a part of the science.... He tries, in his investigations of transformations, to penetrate to the very heart of the bonds that link unlike elements into a whole, attributing to each of them the inherent ability to enter into a certain number of compounds and attributing the differences in properties to the different way in which the elements are linked together.... Butlerov has embedded this thought of his in all the details of his numerous researches."

Butlerov's theory effected a radical change in the antecedent theoretical views, consistently developing the atomic-molecular doctrine and the notion of the chemical structure of molecules as indicating a definite method - the manner of the mutual linking of the atoms in the molecules At the same time a chemical formula should reflect the chemical structure of the molecule, so that only one formula can be written for any substance, based upon a comprehensive study of its chemical transformations, as Butlerov pointed out in 1861, and upon knowledge of the physical properties of the substance once we have been convinced that it is chemically homogeneous. The theory of radicals and types, the substitution theory, and Gerhardt's unitary system all confined this study to an indication of whether certain groups of atoms (or radicals) - not always the same ones - were present in the compound, or else the substance was assigned to one of the types, which was

a partial indication of its functional chemical groups.

Thus, N. N. Zinin's reaction (1842), involving the reduction of nitrobenzene to aniline, emphasized the special nature of the nitro and amino groups and the stability of the phenyl radical. Like the metalepsy involved in the synthesis of chlorine derivatives, the celebrated Zinin reaction exhibits the substitution of hydrogen atoms for oxygen atoms. Though the substitution reaction gave some hint of the "constitution" of a substance, the usefulness of the older theories was chiefly limited to a classification of organic compounds.

The doctrine of valency, which also served as the basis for D. I. Mendeleev's periodic table, represented a great achievement of the science. The notion of the linkage of atoms into carbon chains and rings (Cowper and Kekule) of itself mapped out no new paths in organic chemistry. There is considerable truth in the words of some chemists of the time (such as Blomstrand) who saw nothing particularly original in the establishment of the methane type (by Kekulé), as compared to the derivation of formulas from carbonic acid (by Kolbe), or in the recognition of the possibility that carbon atoms are linked together and with other atoms. It was the Butlerov doctrine that was a genuinely scientific theory

The comparatively rapid establishment of the theory of chemical structure in the science resulted from the study of isomerism, in particular Butlerov and Markovnikov showed how instances of isomerism and metamerism could be inferred with faultless accuracy, using these terms in the precise meanings given them by V. V. Markovnikov [27]. They proved the existence of branched carbon skeletons (isomerism of butane and isobutane, etc.) and of cyclic forms. In 1865 Kekulé advanced a ring structure for benzene. In 1869 Butlerov recognised that his own dioxymethylene was a trimer of formaldehyde and assigned it a cyclic structure, posing the problem of polymethylene rings, especially those with three-membered rings, a year later (1870) [16]. Butlerov's pupils (G. G. Gustavson, F. M. Flavitsky, E. E. Vagner, and others) played a major part in research on the group of polymethylene derivatives.

Only after chemists had begun to apply Butlerov's theory of chemical structure consistently did the problem of stereoisomerism arise, the solution of which Butlerov had temporarily put off in 1861. Stereochemistry must be regarded as a further extension of the structure theory, this isomerism being caused by the three-dimensional arrangement of atoms within the molecule.

Considering the study of isomerism and isomeric transformations to be of special importance, Butlerov introduced dynamical concepts of molecular structure into the science. We know that Butlerov himself and his pupils, particularly A. E. Favorsky (1860-1945), made many valuable contributions to the investigation of molecular rearrangements such as the pinacol rearrangement (1874).

His paper "On the formation of urea" (1862) presented a new concept of equilibrium isomerism, which later came to be called tautomerism and desmotropism. Giving two formulas each for cyanic acid and urea, Butlerov wrote: "If the chemical structure of cyanic acid is represented by the first formula (hydrogen attached to the oxygen—S.D.), the second formula (hydrogen attached to the nitrogen—S.D.) possibly represents a structural phase that exists, though only transitionally," in chemical transormations. The theory of unstable compounds that are readily isomerized is set forth at greater length in Butlerov's 1877 paper on isobutylene (αi-isobutylene) and in his 1879 speech [38]. The first striking syntheses of tautomeric substances were made by A.M.Butlerov in 1870 and by A.P.Eltekov in 1877, using vinyl ethers [42].

In some sources in the literature the discovery of the phenomenon of tautomerism

is wrongly credited to von Laar who proposed the term 'tautomerism." Buterlov did not suggest a new term, as he regarded this as a phenomenon of equilibrium isomerism. Von Laar's views of tautomerism as an oscillation phenomenon (the unceasing shift of the hydrogen atom from one side to the other) and his acceptance of a multistructurality for a single substance are fundamentally wrong. There is something in common between von Laar's notions and Kekulé's view of the oscillation of the multiple bonds in benzene, which are also echoes of the earlier views of Gerhardt and Kekulé on the multiplicity of formulas. Kekulé usually cited the nonexistence of two ortho isomers of benzene as a formal confirmation of the oscillation hypothesis. The structure of benzene is a moot point even today, although the ring structure of its molecule has been proved.

The oscillation hypothesis of von Laar and Kekulé is echoed in part by the conclusions of the groundless idealistic "theory" of resonance and the related concept of mesomerism (Ingold). A basic absurdity is tolerated in these "theories": they postulate imaginary, nonexistent structures, which do not shift from one to another, but which are superposed upon each other within a single molecule (superposition of imaginary structures) and are supposed to be in resonance. Resonance does not exist as a physical phenomenon. The theory of resonance has made its way into our Soviet literature because of the erroneous notion of some chemists and physicists that the "resonance theory" stems from the data of quantum mechanics, because of an intolerable inattention to the conclusions of the theory of chemical structure, and because of an uncritical approach to foreign science, in which Machian and idealistic views are frequently encountered by now.

An important aspect of Butlerov's theory of chemical structure and a corollary of its major premises is the problem of the mutual influences between atoms within molecules, which is of such great significance that it may be regarded as the doctrine of atomic interaction. It was first expounded [8] by Butlerov in his book "Introduction to the special study of organic chemistry" and in Markovnikov's doctoral dissertation (1869), and was extended considerably in subsequent papers by Markovnikov, A. M. Zaitsev, and other chemists of ours. The Markovnikov and Zaitsev rules are common knowledge.

Any generalization covering the phenomena involved in the interaction between atoms and groups within molecules encounters particular difficulties stemming from the great complexity of the problem, although considerable valuable and precise data have been accumulated by now.

The shedding of light upon the interactions of atoms and atomic groups within molecules is closely bound up with the expansion of our knowledge of the nature of chemical affinity. In his very first papers and in many others, A. M. Butlerov called attention to the great importance of correct notions of the chemical bond in chemical theory. In his manual on organic chemistry (1864), Butlerov describes the heat, light, and electrical phenomena occurring in chemical reactions. Ya. K. Syrkin and M. E. Dyatkina are quite wrong in asserting [43] the formal nature of the structure theory and contrasting it with the electrochemical theory of Berzelius, which is alleged to be superior to the theory of chemical structure. It must be said that the theory of chemical structure is presented in their book in a distorted form, while Butlerov's name is not even mentioned; this is not surprising, since the authors considered the false "theory of resonance" to be the highest achievement of science. Berzelius's theory of the fixed bipolarity of atoms, which is firmly welded to the radical theory, did not live long in science, not only because the original theory of radicals fail to account for newly discovered facts (metalepsy) as far back as the forties of the last century, but was itself a crude, highly approximate outline of chemical affinity.

In 1864 Butlerov comments [5] on the importance of the relationship between the chemical action of electricity and the concept of atomicity, which is now of such importance in chemical theory. He returns to the problem of thermal phenomena again and again, discussing the mechanical theory of chemical action. He asserts (in 1864) that the concept of chemical compounds had made great advances since the era of the electrochemical theory, having been changed substantially as a result of the development of the mechanical theory of heat. In 1879 he states [33] that a universal chemical theory will be formulated when we shall know more about the nature of chemical energy, the very essence of atomic motion.

There is no doubt that the doctrine of the mutual interaction of atoms and atomic groups has assisted in the development of electronic concepts in organic chemistry. It may be expected that we shall be able to derive more general laws governing the mutual interactions between atoms and atomic groups within molecules in the light of these concepts.

In working out the theory of the mutual interactions between atoms and atomic groups, and in the electronic interpretations of these phenomena, which is the next major problem facing chemistry and physics, allowance must be made for the role of the reagent and the other reaction conditions

There were differences of form, and of content to some extent, in the writing of chemical formulas during the period when the theory of radicals and types prevailed Chemical formulas were given a wholly new content, a different meaning and significance, in Butlerov's theory of chemical structure, although their outward appearance as written in the sixties differed from their appearance at the beginning of the seventies, when Butlerov definitely adopted multiple bonds in formulas (in 1870). Butlerov regarded the representation method used in formulas as of minor importance He wrote in 1885 [48] When we remember that what matters is not the form, but the concept, the idea, and bear in mind that the formulas representing isomerism must logically express the actual particles, i.e., certain chemical relationships existing within them, we are readily convinced that any way of writing them may be good, provided it expresses these relationships satisfactorily What matters is obviously not the dots, lines, parentheses, or the horizontal or vertical arrangement of these symbols ....." O.A.Reutov was quite wrong [44] in regarding these words as evidence of an inconsistency in Butlerov's assertions and as an alledged use of the doubtful criterion of convenience.

The theory of chemical structure has been the dominant theory in organic chemistry for 90 years. Proving itself to be a truly scientific theory in the Marxist-Leninist sense of the term, and objectively disclosing the chemical relationships and phenomena existing within molecules, Butlerov s theory is characterized by great perceptional and regenerative power

Many of Butlerov's discoveries, which supported his predictions based upon the theory of chemical structure met with no practical application in our country under Czarism. They made their appearance in production during the era of the remarkable Stalin Five-Year Plans of the USSR's national economy This is a striking example of the bond between, the unity of, theory and practice.

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THE DISTRIBUTION OF MECHANICAL AND MAGNETIC MOMENTS OF NUCLEI IN THE PERIODIC SYSTEM OF GROUPS OF ISOTOPES

E.P.Ozhigov

The present paper has as its objective a discussion of the empirical laws and the uncovering of some rules governing the distribution of mechanical and magnetic moments of nuclei in the periodic system of groups of isotopes.

In the appended table of the periodic system of isotope groups we have listed all the most reliable data on the mechanical and magnetic moments of nuclei published by Dorfman. The mechanical moments are stated in $\frac{h}{2\pi}$ units, while the magnetic moments are stated in nuclear magnetons, $\mu_B = 5.0493 \cdot 10^{-24}$ ergs per gauss.

Now let us consider some behavior patterns as related to the constitution of element nuclei.

a) Mechanical and magnetic moments of nuclei with an even number of protons and an even number of neutrons.

Analysis of the available experimental data on isotopes of this nuclear constitution indicates unmistakably that the He^4, C^{12}, O^{16}, S^{32}, Se^{180} nuclei have $I = 0$ and $\mu = 0$.

No other nuclei of this type exhibit any perceptible hyperfine structure, though it is not impossible that some nuclei possess an extremely small magnetic moment, in some cases μ equaling 0. The least research has been done on this group of nuclei.

In accordance with the principle underlying the construction of the periodic system of isotopes groups, nuclei of this constitution will be classed as isotopes with even atomic numbers.

b) Mechanical and magnetic moments of nuclei with an even number of protons and an odd number of neutrons.

About 25 nuclei with this composition have been investigated by now. The mechanical moment of the nuclei varies within a rather wide range, from 9/2 to $\frac{1}{2}$. The magnetic moments are either less than unity or negative. Nuclei of this constitution will likewise be classed as isotopes with even atomic numbers.

c) Mechanical and magnetic moments of nuclei with even N and odd z. This is the group of nuclei on which the most research has been done. In most instances their magnetic moments are greater than one, ranging from 5.6 to -0.19. This group of nuclei is classed as isotopes with odd atomic numbers.

This group is an example of what was shown by Hund [1] some time ago: that the distribution of the I values does not contradict the hypothesis of nuclear shells.

The curve of the variation in the mechanical moments of these nuclei with the number of protons they contain (their atomic number) cited by Dorfman bears this out.

" The progressive filling of the 1s, 2p, 3d, 4f, 5g, etc. shells enables us to observe at what proton number it is likely that a given state will occur. For example, if the first two protons fill the 1s shell, the third electron should occupy the 2p level, so that I = 3/2 cannot occur earlier than z = 3(Li^7). As a matter of fact, Li^7 has an I = 3/2. A state with I = 5/2 cannot occur before the two 1s and six 2p levels are filled. The value of I = 5/2 occurs for the first time in the element with z = 13, i.e., z >8, in the Al^{27} nucleus. The state in which I = 7/2 cannot appear, according to this plan, before the two 1s, the six 2p, the 10 3d, and two 1f levels have been filled, i.e , not before z = 2 + 6 + 10 + 2=20. As a matter of fact, I = 7/2 occurs for the first time in the element whose z = 21, corresponding to a 4f shell. The 5g state with I = 9/2 must therefore occur after the 4f shell has been filled with 14 protons and the 3p shell has been filled with 6 protons. That means that I = 9/2 cannot occur in an element whose z is less than 40. In fact, I = 9/2 occurs for the first time at z = 41 in Ni^{93}. This is therefore, a weighty confirmation of the hypothesis of nuclear shells. Beyond this point, however, the experimental values of I do not agree with the outline. I should be 11/2 for an element with a z in excess of 68, which would represent the filling of the 6h shell. As a matter of fact, however, it is only at Lu^{176} that we find I >14/2, the others having I ≤ 9/2. But this discrepancy between the outline and experiment is hardly a serious argument against the outline. For the number of neutrons begins to exceed the number of protons considerably in elements whose z is greater than 50. This probably distorts the field within the nucleus to such an extent that the alternation of the levels derived from the model of the "potential cage ceases to correspond to reality, as has been pointed out already."

The quantum outline of nuclear shells is also confirmed in nuclei possessing a different strucutre. It is worthy of note that the change in the mechanical moments with levels is reflected rather convincingly in the periodic system of isotope groups.

d) Mechanical and magnetic moments of nuclei possessing an odd number of protons and an odd number of neutrons.

There are no more than 6 nuclei in this group. The light nuclei of this type contain an even number of protons and neutrons. Experiment indicates that the H^2, Li^6, B^{10} and N^{14} nuclei possess a moment I = 1. In k^{40} the mechanical moment is 4m while in Lu^{176} it exceeds 7. The magnetic moment ranges from 3.8 (Lu^{176}) to -1.290 (K^{40}).

Nuclei of this type are likewise of interest from the standpoint of the way in which the nuclear levels are filled.

In discussing all the data it must be borne in mind that there is no simple relationship between the values of I and μ . Still, certain empirical behavior patterns may be found in the numerical values of the magnetic moments:

a) In every nucleus possessing an odd proton, the difference between μ_{max} and μ_{min} is about μ_p; for a given I.

b) In nuclei possessing an odd neutron, the difference between μ_{max} and μ_{min} is about 1μN. for a given I. Contemporary science has not yet learned the real significance of this behavior pattern.

The periodic system of isotope groups reveals still other patterns of behavior, which bear out the quantum scheme of constituting nuclear shells. One of these patterns may be formulated thus: In series of isotopes of two adjacent periods, nuclei of similar structure have mechanical and magnetic moments, the numerical values of which are close together and are given by adjacent sequences

of numbers. The second and third short periods are the most striking examples of this. In these periods the difference between the mass numbers of the isotope-analogs is 16. If we arrange the isotopes of these periods with their mechanical and magnetic moments in the order of their periodicity, we get a series of periodically repeating numbers. The values of the mechanical and magnetic moments of the isotopes for which these values have been determined are listed in Table 1.

TABLE 1

Periods	Value	GROUPS 1		2	3		4		5		6	7	
1	Isotopes	Li^6	Li^7	Be^9	B^{10}	B^{11}	C^{12}	C^{13}	N^{14}	N^{15}	O^{16}	F^{19}	None
	I	1	3/2	3/2	1	3/2	0	1/2	1	1/2	0	1/2	None
	μ	0.821	3.253	-1.17	0.598	2.68	0	0.701	0.403	0.280	0	2.62	None
2	Isotopes	None	Na^{23}	Mg^{25}	None	Al^{27}	Si^{28}	Si^{29}	None	P^{31}	S^{32}	Cl^{35}	Cl^{37}
	I	None	3/2	-	None	5/2	0	-	None	1/2	0	3/2	3/2
	μ	None	2.215	-	None	3.63	0	-	None	1.131	0	1.36	1.13

The periodically repeating numbers correspond to a nuclear series constructed along the lines of helio groups: Q, Q + 1, Q + 2, Q + 3. This may be seen in the C^{12} to O^{16} and Si^{28} to S^{32} isotope series. We do not have much quantitative data on mechanical and magnetic moments at the present time, but nevertheless we need not doubt that the values of the mechanical and magnetic moments can be predicted from the existent behavior patterns for several isotopes. A zero value (or a value close to zero) may be pre-supposed for the mechanical and magnetic moments of the isotopes Mg^{24}, Ne^{20}, S^{36}, and A^{36}. The magnetic moment must be small or even negative for the isotopes Mg^{25}, Si^{29}, etc.

When isotopes of similar structure are grouped together, a definite periodicity may be observed. The mechanical and magnetic moments of nuclei with odd z and odd N are arranged in Table 2.

In Group 1 we observe that the mechanical moments of the nucleus increase from Li^7 to Cs^{133}, while the magnetic moments decrease to some minimum value and then rise again. In the subordinate subgroup of Group 1, the smallest values of the mechanical and magnetic moments are exhibited by the nuclei of the isotopes of silver. In Group 3, on the other hand, the mechanical and magnetic moments rise irregularly, attaining a maximum in Period 5. In Group 5, the increase in the mechanical and magnetic nuclear moments likewise is greatest in Period 5. In Group 7, the mechanical moments increase regularly to the end of the periodic system. The magnetic moments fall to a certain minimum value, after which they rise again. In the subordinate subgroup (nuclei of the manganese and rhenium isotopes), the mechanical and magnetic moments are almost the same

TABLE 2

Arrangement in a Periodic Table of Isotopes of the Mechanical and Magnetic Moments of Nuclei with Odd z and Odd N.

Periods	Groups 1		2		5		7	
	Principal subgroup	Subordinate subgroup	Principal subgroup	Subordinate subgroup	Principal subgroup	Subordinate subgroup	Principal subgroup	Subordinate subgroup
1 I =	-	-	-	-	-	-	H_1	-
μ =	-	-	-	-	-	-	1/2	-
	-	-	-	-	-	-	2.789	-
2 I =	Li^7	-	B^{11}	-	N^{15}	-	F^{19}	-
μ =	3/2	-	3/2	-	1/2	-	1/2	-
	3.253	-	2.68	-	0.218	-	2.62	-
3 I =	Na^{23}	-	Al^{27}	-	P^{31}	-	Cl^{35} Cl^{37}	-
μ =	3/2	-	5/2	-	1/2	-	3/2 3/2	-
	2.215	-	3.63	-	1.133	-	1.36 1.13	-
4 I =	K^{39} K^{41}	Cu^{63} Cu^{65}	Ga^{69} Ga^{71}	Sc^{45}	As^{75}	V^{51}	Br^{79} Br^{81}	Mn 55
μ =	3/2 3/2	3/2 3/2	3/2 3/2	7/2	3/2	7/2	3/2 -	5/2
	0.391 0.215	2.226 2.385	2.061 2.561	4.6	1.5	?	2.10 2.27	3
5 I =	Rb^{85} Rb^{87}	Ag^{107} Ag^{109}	In^{113} In^{115}	Y^{89}	Sb^{121} Sb^{123}	Nb^{91}	I^{127}	Tc^{99}
μ =	5/2 3/2	1/2 1/2	9/2 9/2	?	5/2 7/2	9/2	5/2	?
	1.34 2.733	-0.1 -0.2	6 4 5.43	?	3.7 2.8	5.3	2.812	?
6 I =	Cs^{133}	Au^{197}	Tl^{203} Tl^{205}	La^{139}	Bi^{209}	Ta^{181}	At	Re^{185} Re^{187}
μ =	7/2	3/2	1/2 1/2	7/2	9/2	7/2	?	5/2 5/2
	2.55	0.2	1.628 1.644	2.76	3.45	2.1	?	3.3 3.3

SUMMARY

1. Notwithstanding the comparatively sparse data on the mechanical and magnetic moments of nuclei, we can trace their regular arrangement in the periodic system of isotope groups as functions of the odd and even atomic numbers, periods and groups.

2. Elements with odd numbers are characterized by the wide range of variation of the magnetic moments, which are as high as +5.5, whereas the magnetic moments do not rise even as high as plus one in isotopes with even numbers.

3. Periods and groups of similar nuclei have mechanical and magnetic moments that are of the same approximate size, while groups whose atomic numbers differ by being odd and even exhibit marked differences in these values.

4. The quantum outline for the constitution of nuclear shells is strikingly borne out in the periodic system of isotope groups.

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Received August 14, 1949.

AN INVESTIGATION OF HYDRATES BY THE HYDRIDE METHOD

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As we know, the structure of many hydrates and crystal hydrates has not been very clear down to very recently. Contradictory opinions are often found in the periodical and specialized literature on the nature of a given hydrate. In some cases the chemical formulas merely represent a given hydrate schematically without representing its actual composition, not to mention its chemical behavior.

The present research has had as its objective an attempt to shed light upon the nature of the hydroxides of iron, copper gold, aluminum, and a few other elements, as well as of boric and periodic acids, by comparing our own experimental data secured by using the hydride method to determine water with the data to be found in the literature on investigations of these hydrates by other methods.

The hydride method employed by us to determine the stability of hydrates, originally developed by A. G. Elitsur to determine water in coordination aqua compounds [1], is based upon the extraction of water from hydrates by pyridine and reacting it with hydrides of the alkali earth metals to evolve hydrogen, the percentage of water in the hydrate being found from the volume of the latter. The part played by the active medium (pyridine) in this method is mainly its chemical reaction with the water in the compound under test (especially via substitution in the formation of a complex ion), the hydrate serving to displace the hydrate $\rightleftarrows$ pyridine hydrate equilibrium continuously. This method makes it possible to study hydrates at low temperatures, often at room temperature, without destroying their internal structure as is the case in the thermal method and without running the risk of splitting out other, easily volatile or easily decomposable structural constituents (as, for instance, the evolution of oxygen, iodic anhydride, and water when periodic acid is heated). The method is specific for water, hydroxyl groups not being determined by this method. This method has made possible a different approach to the study of hydrates.

The following hydrates have been investigated in the present research: copper hydroxide $Cu(OH)_2$, auric hydroxide $Au(OH)_3$, cadmium hydroxide $Cd(OH)_2$, aluminum hydroxide $Al(OH)_3$, gallium hydroxide $Ga(OH)_3$, chromic hydroxide $Cr(OH)_3$, ferric hydroxide $Fe(OH)_3$, and nickel hydroxide $Ni(OH)_2$, in addition to orthoboric acid H_3BO_3, periodic acid $HIO_4 \cdot 2H_2O$ (H_5IO_6), and one of the organic hydrates: chloral hydrate $CCl_3CH(OH)_2$.

All these hydrates with the exception of boric acid, periodic acid, and chloral hydrate, possess a number of typical features which sharply distinguish them from the corresponding compounds of the alkali and alkali-earth metals. One of the distinctive features of this group of hydrates, for example, is their nearly total insolubility in water. Another important difference between these hydroxides and the corresponding hydrates of the alkali and alkali-earth metals is that nearly all of them look like hydrogels and turn into horny masses when dried. Only a few of the crystaline hydroxides have been described in this group. They include some natural hydrates, such as aluminum hydroxide (hydrar-

gillite), goethite – a hydrated oxide of iron, and a few others.

The results of our determination of water in the specified hydrates by the hydride method are given below.

1) Cupric Hydroxide – $Cu(OH)_2$

Cupric hydroxide, thrown down as an amorphous precipitate when solutions of divalent copper salts are reacted with an excess of alkali, is extremely unstable thermally, giving off water when gently heated. It is completely decomposed: within 9 months at 15°, within 86 hours at 30°, and within 45 hours at 45°.

This hydrate is progressively dehydrated even under water, yielding a black hydrate: $3CuO \cdot H_2O$. The crystalline form of the hydrate is more stable, and can be heated to 100° without decomposing. The properties of cupric hydroxide, especially its undergoing spontaneous dehydration, depend largely upon how it is prepared. A comprehensive paper by Kohlschutter and Tuscher is devoted to the explanation of this fact [2]. Stoichiometrically, the dehydration process may be represented by the following equation: $Cu(OH)_2 \rightarrow CuO + H_2O$. This process might be represented by the cited equation, according to these authors, provided it occurred within a substance separated into molecules somehow or other. In actuality, however, the process takes place in giant complex molecules, united into colloidal particles. The degree of dispersion of these particles, these authors assert, is the decisive factor in setting off the reaction in which water is split out, this reaction being conceivable as a neutralization reaction that occurs intermolecularly. The cupric hydroxide, $Cu(OH)_2$, which is an amphoteric compound, gives off hydrogen ions and hydroxyl ions, which then combine to form molecules of water as follows:

$$Cu(OH)_2 \rightarrow Cu^{\cdot\cdot} + 2OH^{'},$$
$$Cu(OH)_2 \rightarrow CuO_2^{''} + 2H^{\cdot},$$
$$2H^{\cdot} + 2OH^{'} \rightarrow 2H_2O,$$
$$Cu^{\cdot\cdot} + CuO_2^{''} \rightarrow 2CuO.$$

The available experimental data indicate that the onset and course of the reactions are likewise affected by the arrangement of the particles alongside one another, i.e., by the structure of the solid phase. The crystallochemical data on the structure of crystalline hydrates indicate that many of them form a layer lattice of the cadmium iodide type, in which the hydroxyl groups are arranged in layers, and that the hydrogen ions tend to migrate, which explains the formation of water [15].

We have investigated one sample of "c.p." cupric hydroxide and two samples prepared in the laboratory by the Bottger method [3]. Our tests have shown that water cannot be determined by the hydride method in this hydrate, notwithstanding its extreme thermal instability (the amount of water evolved is negligible: 2, 0.9, and 2.2%, and may be attributed to hygroscopic moisture). When we remember that hydroxyl groups cannot be determined by this method, this fact confirms, on the one hand, the correctness of the formula attributed to it, $Cu(OH)_2$, and on the other, the opinion of the authors cited concerning the probable cause of the spontaneous decomposition of this hydrate.

2) Auric Hydroxide – $Au(OH)_3$ – Auric Acid

Auric hydroxide was prepared by gradually adding dilute alkali solutions to a solution of auric chloride, $AuCl_3$. Auric hydroxide is amphoteric, its acidic functions being more pronounced than the basic. The salts of auric acid – aurates – are produced from the meta form, $HAuO_2$, and are formed by dissolving the hydrox-

ide in concentrated solutions of strong alkalies.

We tested a product prepared in the laboratory and dried to constant weight in a desiccator above sulfuric acid. We found that auric hydroxide gives off water at 70-73°, the percentage of water evolved in two tests being 7.1% and 8%, respectively, corresponding to one mol of water per mol of the hydrate (the theoretical quantity corresponding to one mol per mol of the hydrate is 7.3%). When we remember that the salts of auric acid are produced from the meta form, $HAuO_2$, we may consider $Au(OH)_3$ formally as a monohydrate of meta-auric acid, $HAuO_2 \cdot H_2O$.

3) Cadmium Hydroxide – $Cd(OH)_2$

This hydrate, secured as a jellylike precipitate by reacting solutions of cadmium salts with solutions of strong alkalies, has pronouncedly basic properties. The samples tested by us, prepared in the laboratory and desiccated to constant weight in a desiccator above sulfuric acid, whose purity was checked by calcining them to the oxide CdO, indicated that no water can be determined in this hydrate by the hydride method.

4) Aluminum Hydroxide – $Al(OH)_3$

Experiments conducted by Willstatter and Kraut [4] confirm the previously observed variation of the composition and chemical properties of aluminum hydroxide with the method of its preparation. It would be wrong, however, to deny the existence of such compounds as $Al(OH)_3$ and $AlO(OH)$. Their existence had been demonstrated earlier in the researches of Hutting and Witgenstein [5]. Thus, when the aluminum hydroxide is forced to settle out as a precipitate, the gel formed initially turns into an $Al(OH)_3$ powder upon aging, possessing the definite X-ray picture of a crystalline powder. As for the hydrates deposited from hot solutions with ammonia, they have the composition of $AlO(OH)$ and exhibit the X-ray picture of bauxite. Other natural hydrates, such as diaspore, $AlO(OH)$, and hydrargillite, $Al(OH)_3$, are also crystalline aluminum hydroxides. The problem of the number and nature of the water bonds in precipitated aluminum hydroxide is extremely complicated because of its colloidal character, remaining unsolved until very recently. At the time of the researches of Bemmelen and Zsigmondy [6, 10] on the variation of the percentage of water in the gels with the vapor pressure in the gas phase, the gels of hydrous aluminum oxide were regarded not as hydroxides, but merely as oxides that contained adsorbed water.

Subsequent researches disproved these assumptions. Willstatter and Kraut [4] were able to isolate (at $\underline{t}$ = 17°) a hydrate with a high percentage of water, its composition being $2Al(OH)_3 \cdot H_2O$, which lost water at room temperature, turning into a stable hydrate with the composition of $Al(OH)_3$. When heated rapidly, the ortho hydrates are transformed into the monohydrate $AlO(OH)$, without passing through intermediate stages, the latter turning into aluminum oxide, Al_2O_3. Loewe [7] secured a stable hydrate with the composition of $Al_2O(OH)_4$.

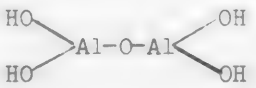
At the present time the possible existence of all these hydrates has been confirmed by the researches of P. T. Danilchenko, who applied physico-chemical analysis to a study of amorphous hydroxides (dehydration at the solid – liquid boundary surface [16, 17]). He and his associates have shown that dehydration of the hydrogel of aluminum oxide takes place as follows: $2Al_2O_3 \cdot 6H_2O \rightarrow 2Al_2O_3 \cdot 5H_2O \rightarrow 2Al_2O_3 \cdot 4H_2O \rightarrow 2Al_2O_3 \cdot 3H_2O \rightarrow 2Al_2O_3 \cdot 2H_2O \rightarrow 2Al_2O_3 \cdot H_2O \rightarrow Al_2O_3$.

In its chemical behavior aluminum hydroxide is amphoteric. It is characteristic that the only aluminates known correspond to the hydrate with the composition of $AlO(OH)$ or $HAlO_2$.

We have investigated a sample prepared in the laboratory by the Schmidt method [8]. The resultant hydrate was desiccated for a long time (a month) in an exsiccator above sulfuric acid. Calcination to the oxide - Al_2O_3 - made by way of a check indicated that the percentage of water given off was 34.3% (the theoretical content being 34.6% if we assume that the hydrate has the formula of $Al(OH)_3$).

Two determinations by the hydrate method gave the percentage of water eliminated as 10.6 and 11.1%, respectively. Besides, in the hydride method dehydration sets in at room temperature, splitting out one mol of water per two mols of the hydrate (theoretically, we should have got 1.5%), representing a compound with the composition of $Al_2O(OH)_4$, previously secured by Loewe, the possibility of whose existence had been confirmed by the researches of P. T. Danilchenko.

The hydrate $Al_2O_3 \cdot 2H_2O$ we secured could have been assigned the following formula:



but this formula does not accord with its properties (such as the formation of meta-aluminates) giving us reason to suppose that the hydrate with the composition of $Al_2O_3 \cdot 3H_2O$ is a compound of more complex structure.

5) Gallium Hydroxide - $Ga(OH)_3$

Gallium hydroxide is precipitated as a gel that is insoluble in water, but is readily soluble in alkalies, acids, and a concentrated solution of ammonia when solutions of alkalies are reacted with solutions of its salts. Its chemical properties indicate that $Ga(OH)_3$ is a rare example of an electrolyte that is nearly perfectly amphoteric, the following are the measured values of the second and third dissociation constants of the acid and basic type:

$$K_2 = 5.10^{-11}, \quad K_3 = 2.10^{-12},$$
$$K_2 = 2.10^{-11}, \quad K_3 = 4.10^{-12} [9]$$

We tested a sample of $Ga(OH)_3$ supplied by the Institute of Fine Chemicals Technology. It was dried out in a desiccator above sulfuric acid for 12 days and then calcined, after which its water content was 23.9% (the theoretical value is 24.5%).

The percentage of water, as determined by us by the hydride method, was found to be 14.2%, equivalent to one mol per mol of the hydrate (theoretically this figure should be 14.8%). Dehydration sets in at room temperature when this method is employed. Thus, gallium hydroxide, like auric hydroxide, behaves like a monohydrate of metagallic acid: $HGaO_2 \cdot H_2O$.

6) Chromic Hydroxide - $Cr(OH)_3$

Chromic hydroxide is usually prepared by reacting a solution of a chromium salt with a solution of ammonia, the hydroxide settling out as a gray-blue amorphous precipitate that is slightly soluble in water. The percentage of water in chromium hydroxides varies widely, depending upon the method of preparation and the subsequent processing. There are very many references to this in the literature, which are often contradictory. Thus, drying at 100° yields a hydrate whose composition may be represented schematically by the formula $Cr_2O_3 \cdot 4H_2O$,

turning into the hydrate $Cr_2O_3 \cdot 7H_2O$ when it is kept in moist air and into the hydrate $Cr_2O_3 \cdot 3H_2O$ when gently calcined. The (green) hydrate $Cr_2O_3 \cdot 5H_2O$ has also been prepared. The hydrate $Cr_2O_3 \cdot 8H_2O$ settled out of a chromium salt solution in the cold, giving off water without changing color when heated to 110°, thus turning into the hydrate $Cr_2O_3 \cdot 6H_2O$; when this hydrate is desiccated above sulfuric acid, the hydrate $Cr_2O_3 \cdot 5H_2O$ is formed, and when it is dried in vacuum, we get $Cr_2O_3 \cdot 4H_2O$. The hydrate $Cr_2O_3 \cdot H_2O$ was secured by keeping one of the hydrates mentioned above in a current of anhydrous hydrogen for 6 days at 200°.

Chromic hydroxide is markedly amphoteric. We obtained chemically pure samples: dark-green and light-green, both samples being dried to constant weight by keeping them in a desiccator above sulfuric acid. A check calcination to chromic oxide indicated that the former hydrate had the composition of $Cr_2O_3 \cdot 7H_2O$ and the second that of $Cr_2O_3 \cdot 6H_2O$. Dehydration by the hydride method sets in at 35-40°, continuing to the hydrate $Cr_2O_3 \cdot 4H_2O$ in both instances, this hydrate apparently being most stable. The same results were secured when the two samples were dried for a long time at 105° in a drying cabinet.

7) Ferric Hydroxide – $Fe(OH)_3$

Opinions differ widely regarding the nature of ferric hydroxide. It follows from Bemmelen's paper [10], for instance, that the components Fe_2O_3 and H_2O do not form a chemical compound of definite composition with a definite water vapor pressure above it, but rather an adsorption compound of indeterminate composition, depending upon the temperature, the vapor pressure, the structure of the gel, and the manner in which it was produced, which may vary continuously.

N. S. Kurnakov and E. Ya. Rode [11] investigated the natural hydroxides of iron by the heating-curve method, concluding that there is no series of ferric hydroxides with a definite stoichiometric percentage of water. The monohydrate $Fe_2O_3 \cdot H_2O$ is apparently a natural compound of definite composition, but even this requires further confirmation. Other investigations of ferric hydroxide by different methods: desiccation with acetone, freezing, X-ray analysis, and the like, yielded the same conclusions. Later concepts regarding the structure of ferric hydroxide may be summarized in general as follows: the gel is a solidified base of spongy structure, permeated by a multiplicity of fine capillaries filled with water; the total water content of the freshly prepared preparation is a variable quantity, dependent upon the structure of the gel.

We tested two samples by the hydride method that had first been reduced to constant weight in a desiccator above sulfuric acid. Our investigation showed that water begins to be given off at room temperature. One sample lost 17.6% in weight when calcined to constant weight over a low Bunsen flame, losing 13.7% by the hydride method. The second sample lost 16% in calcination, and 12.7% by the hydride method. Thus, the tested samples had neither the composition of $Fe(OH)_3$ (in which the theoretical water content should be 25.2%) nor that of $Fe_2O_3 \cdot H_2O$ (in which the theoretical water content should be 10.0%). The difference between the amount of water evolved thermally and that measured by the hydride method was evidently attributable to the presence of basic salts.

8) Nickelous Hydroxide – $Ni(OH)_2$

Two determinations of the water in this compound hydroxide indicated that the hydride method cannot be employed to determine the percentage of water in this hydrate.

9) Orthoboric Acid - H_3BO_3

Boric acid is ordinarily prepared by treated natural borates with acids at high temperature. When it is heated it loses water, turning (at 107°) into metaboric acid (HBO_2), then into tetraboric acid ($H_2B_4O_7$), and finally into boric anhydride. According to A. V. Nikolaev [12], no metaboric acid, with the formula of HBO_2, is produced in the dehydration of the orthohydrate, since study of the dehydration curves indicates that it first loses one molecule of water per two molecules of the ortho acid, yielding the diboric acid $H_4B_2O_5$, the latter losing one molecule of water to form the diboric acid $H_2B_2O_4$. The electrolytic dissociation of the hydrate $(BOH)_3$ in solution is of the acidic type. Because of the extreme weakness of the acid, however, only one hydrogen ion is detached from each molecule, so that nothing but monosubstituted salts can be formed in the solution. In nature and in the laboratory we do not encounter salts of the ortho form (H_3BO_3), but rather salts of polyboric acids with the general formula of $xB_2O_3 \cdot yH_2O$, most often tetraboric and metaboric acids. We cannot say in advance whether the borate formed in the solution comes from the ortho-, meta-, or tetraboric acid, inasmuch as all three are precipitated, e.g., $AgBO_2$, $Ca(H_2BO_3)_2$, and $Na_2B_4O_7$, for ions of all types that can be produced by boric acid are mixed together in a solution of boric acid and its salts.

Our preliminary experiments indicated that anhydrous acids, even such strong acids (compared to boric acid) as oxalic acid, $(COOH)_2 \cdot 2H_2O$, and citric acid, $C_3H_4(OH)(COOH)_3 \cdot H_2O$, do not react with calcium hydride when dehydrated with pyridine and dioxane to remove any traces of moisture. When they contain crystallization water, the same acids give all of it up, as seen in Table 1, which lists the data of five determinations (three for oxalic acid and two for citric acid).

TABLE 1

Acid	Weight, grams	Per cent		Remarks
		Theoretical	Experimental	
$(COOH)_2 \cdot 2H_2O$.....	0.1666	28.5	28.2	In dioxane
$(COOH)_2 \cdot 2H_2O$.....	0.1822	28.5	27.9	In pyridine
$(COOH)_2 \cdot 2H_2O$.....	0.1810	28.5	28.0	In pyridine
$C_3H_4(OH)(COOH)_3 \cdot H_2O$.....	0.3181	8.57	8.75	In pyridine
$C_3H_4(OH)(COOH)_3 \cdot H_2O$.....	0.1863	8.57	9.05	In dioxane

We tested a sample of c.p. boric acid. When we calcined some of it to boron oxide, B_2O_3, we found that 44.5% of water was given off (the theoretical quantity being 43.7%).

The results of our determinations of water in orthoboric acid by the hydride method are given in Table 2. (See next page).

Thus, when the water in orthoboric acid was determined, the latter was dehydrated to tetraboric acid at 20°. The first molecule (corresponding to a theoretical percentage of 29.2% of water) was determined quickly, dehydration practically coming to a stop at this point at 16°.

10) Periodic Acid - $HIO_4 \cdot 2H_2O$ (H_5IO_6)

By periodic acid we usually mean its hydrate with two molecules of water ($HIO_4 \cdot 2H_2O$), which consists of colorless prismatic crystals that melt at 130° with partial decomposition. Further heating results in decomposition, yielding water, iodic anhydride (I_2O_5), and oxygen. The determination of water in this

TABLE 2

Test temperature	Medium	Dehydration time	Per cent water		Remarks
			Theoretical	Experimental	
16	Dioxane	3 hours	To HBO_2:29.2	28.7	In every instance dehydration set in at room temperature
16	Pyridine	3 hours	To HBO_2:29.2	29.1	
20		4 hours	To $H_2B_4O_7$:35.4	36.9	
50		4 hours	To $H_2B_4O_7$:35.4	35.6	
85		3 hours	To $H_2B_4O_7$:35.4	36.0	
95		90 min.	To $H_2B_4O_7$:35.4	35.4	

acid by any of the known methods involves great difficulty, because of its instability. The problem of its water content is complicated still further by the fact that it is often a pentabasic acid, forming several neutral and acid salts (such as Ag_5IO_6, $Na_2H_3IO_6$, and KH_4IO_6). For that reason attempts have been made to solve the problem of its water content indirectly. One of these indirect methods is given in the paper by Aggarwal and Singh [13]. By measuring the magnetic susceptibility, these authors concluded that periodic acid contains two mols of water per mol of the anhydrous acid, both in the crystalline state and in solution, and assigned it the formula $HIO_4 \cdot 2H_2O$.

We tested a sample prepared by the Wells method [14] and desiccated above sulfuric acid to constant weight. We found that periodic acid gives up water readily (even at room temperature).

Three determinations yielded the following results: 15.6% at t = 19°; 15.5% at t = 23°; and 15.1% at t = 100°, equivalent to two mols of water per mol of acid (the theoretical percentage of water should have been 15.8%). This result is in full agreement with the conclusions of the authors cited and corroborates the formula they give for it: $HIO_4 \cdot 2H_2O$. The question of why periodic acid can act as a pentabasic acid remains an open one.

11) Chloral Hydrate - $CCl_3CH(OH)_2$

We know that the hydrates that could be formed by the addition of water to an aldehyde group with two hydroxyl groups attached to a single carbon atom, cannot be isolated, water being split out at once; exceptions to this rule are the compounds in which the carbon atom adjacent to the aldehyde group is attached to another aldehyde group (such as glyoxal hydrate - $(OH)_2CH \cdot CH(OH)_2$), or to a carboxyl group (such as glyoxylic acid hydrate - $COOH \cdot CH(OH)_2$), or, lastly, when the carbon atom adjoining an aldehyde group is attached to chlorine (or bromine) atoms. Chloral hydrate - $CCl_3CH(OH)_2$ - is one of these latter compounds. All these compounds are fairly stable hydrates. Chloral hydrate is only partially broken down into chloral and water at its boiling point. Its chemical properties (like those of other chlorinated acetaldehydes) indicate, as it were, that the water it contains is not crystallization water (i.e., combined by means of auxiliary valence bonds or by the binding forces of the crystal lattice) but is combined with it chemically. Chloral hydrate, for example, does not exhibit the typical aldehyde reaction with fuchsinsulfurous acid, so that we may assign it the well-known formula $CCl_3CH(OH)_2$, indicating that it is a rare example of a glycol with two hydroxyl groups attached to a single carbon atom.

Our determinations have revealed, however, that water is undoubtedly present in this compound.

As we see in Table 3, which lists the results of six determinations of water in chloral hydrate, the first four using pyridine and the last two dioxane as the

dehydrating medium, the difference between the theoretical percentage of water (on the assumption that it contains one molecule of water per molecule of chloral) and that found by the method we propose amounts to only tenths of one per cent.

TABLE 3

Weight, grams	Temperature	Volume of hydrogen evolved, ml	Per cent		Remarks
			Theoretical	Experimental	
0.1430	18	21.2	10.9	10.9	Dehydration set in at about 60°
0.2608	17	36.8		10.4	
0.1635	18	24.0		10.7	
0.1692	21	26.1		11.1	
0.1383	19	19.5		10.4	
0.1492	22	21.4		10.6	

These tests thus confirm the undoubted presence of one molecule of water in the chloral hydrate molecule, though the nature of the bond involved is unclear.

In conclusion, we must state that, as far as the hydroxides investigated in this research are concerned, the composition and behavior of some of them (ferric hydroxide and chromic hydroxide) and, possibly, of many others that we have not tested, are not reflected by the schematic formulas cited in the periodical literature as first approximations and in the textbooks for the methodological purposes of simplification and analogy.

Because of their jellylike state, the hydrates we have been discussing, especially the freshly precipitated ones, contain an indeterminate percentage of water. The colloidal nature of most of the hydroxides is, apparently, not fortuitous, but is their peculiar form of stabilization. For a deeper understanding of the nature of the chemical transformations that occur in nature and for their correct interpretation, we must, therefore, shift from the traditional molecular schemes to directly accessible observation and research in the field of larger aggregates of matter.

SUMMARY

Our researches have established the following.

1 Water cannot be determined by the hydride method in hydroxides of divalent metals: $Cu(OH)_2$, $Cd(OH)_2$, and $Ni(OH)_2$.

2. Auric hydroxide, $Au(OH)_3$, evolves one mol of water per mol of the hydrate, so that auric hydroxide, $Au(OH)_3$, may be regarded as a monohydrate of meta-auric acid, i.e., as $HAuO_2 \cdot H_2O$, when it is borne in mind that aurates are formed only in the meta form – $HAuO_2$.

3. One mol of water is found per mol of the hydrate by the hydride method in gallium hydroxide, as in auric hydroxide.

4. In aluminum hydroxide, $Al(OH)_3$, the hydride method indicates that one mol of water is present for every two mols of the hydrate, i.e., dehydration progresses until the hydrate $Al_2O(OH)_4$, which has been isolated in the free state and described in the literature is formed.

5. The dehydration of chromic hydroxide (general formula $Cr_2O_3 \cdot xH_2O$) progresses until the hydrate $Cr_2O_3 \cdot 4H_2O$ is formed, whether the hydride method is

used or it is desiccated in a drying cabinet at 105°; this latter hydrate must be regarded as the most stable of all the hydroxides of chromium.

6. Tests of ferric hydroxide appear to indicate that there is no hydrate of definite composition (such as, say, $Fe(OH)_3$).

7. At temperatures up to 16° orthoboric acid (H_3BO_3) gives off only one mol of water per mol of acid, i.e., it is denydrated to metaboric acid (HBO_2); at temperatures of 16-20° dehydration results in the formation of tetraboric acid, $H_2B_4O_7$.

8. It is very easy to determine the existence of two mols of water per mol of acid, even at room temperature, in periodic acid, by the hydride method, which supports the adoption of the formula $HIO_4 \cdot 2H_2O$ for this acid and fully agrees with the results of the research done on its magnetic susceptibility. The question of why periodic acid behaves like a pentabasic acid remains an open one, however.

9. The hydride method indicates that chloral hydrate contains one molecule of water per molecule of the hydrate. The nature of the bond linking the water to the hydrate is still unclear, however

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Received December 28, 1949.

DOUBLE DECOMPOSITION IN THE ABSENCE OF A SOLVENT

LXX. THE IRREVERSIBLE SALT-PAIR RECIPROCAL SYSTEM OF LITHIUM AND ZINC CHLORIDES AND SULFATES

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The investigation of the formation of coordination compounds when molten salts react together is of considerable theoretical interest. Until recently it was commonly believed that the principal factor governing a double decomposition reaction was the nominal thermal effect of the exchange reaction, the formation of compounds within the system, the nominal thermal effects of whose formation is high, in turn affects the course of the reaction. Examples of this are the adiagonal systems that have been investigated recently in our laboratory.

The literature contains references to a large number of systems in which double salts with common cations or anions are formed. But not much research has been done on systems in which heteroionic compounds are formed. Janecke discovered the double salt $KCl \cdot MgSO_4$ in the $K,Mg||Cl,SO_4$ system [1]. By analogy with the natural kainite $KCl \cdot MgSO_4 \cdot 3H_2O$ we call this salt an anhydrous kainite or simply kainite for short henceforth. O. S. Dombrovsky observed the formation of similar salts in his study of the diagonal sections of the $K,Zn||Cl,SO_4$ systems [2], while A. G. Bergman [3] has found them in the $AgNO_3 - HgI_2$ and other systems. This list might be supplemented by various examples culled from published and as yet unpublished papers.

The tendency of zinc chloride and sulfate to form binary compounds with the chlorides and sulfates of the alkali metals leads us to suppose that a coordination compound will no doubt be formed in the $Me_2Cl_2 + ZnSO_4 \rightleftarrows Me_2SO_4 + ZnCl_2$ systems (where Me is one of the alkali metals). N. P. Luzhnaya and I. P. Vereshchetina [4], in their study of systems consisting of zinc sulfate and chlorides of monovalent metals, have shown by thermal analysis and conductance methods that $ZnSO_4$ forms compounds of the kainite type with many MeX salts (where Me = K, Rb, Cs, and Tl, and X = Cl, Br, and I).

By comparing the results obtained the paper just referred to with the researches in the literature on the reaction of the chlorides and sulfates of the alkali metals with various divalent metals (Mg, Zn, Mn, Cd, Ca, and Pb) N. P. Luzhnaya has shown that the complex ions of the $[XMeSO_4]^-$ type, which make possible the formation of kainites, may be formed only when the generalized moment of the central ion in the complex ion is large enough, compared to the generalized moment of the monovalent ion.

Although the coordination compounds $ZnCl_2 \cdot 2LiCl$ and $ZnCl_2 \cdot ZnSO_4$ are formed in lateral binary systems, we could not expect a lithium kainite to be produced, since, on the one hand, the ionic radius of Li^+, 0.78 Å, is far from the same as those of Na^+, 0.98 Å, or K^+, 1.33 Å, no kainite existing in systems containing Na salts. On the other hand, the equilibrium of the exchange reaction, as we see from our calculation (vide infra), is shifted toward the opposite pairs

$Li_2SO_4 + ZnCl_2$, which cannot give rise to a kainite. Experimental research has confirmed this assumption.

The nominal thermal effect of the exchange reaction in the $LiCl_2 + ZnSO_4 \rightleftarrows Li_2SO_4 + ZnCl_2$ system is rather high, 5.38 Cal per equivalent pair, so that the exchange reaction ought to be sharply shifted toward the right. and the system would be classed as an irreversible reciprocal salt-pair system in the A. G. Bergman classification [5]. Unfortunately, we have been unable to calculate the change in the free energy of this sytem, owing to the absence of any data on the heat capacity of zinc chloride in the literature, as well as the absence of other data.

The present paper is a first report on a series of systems we have investigated: $Li,Zn\|Cl,SO_4$, $Na,Zn\|Cl,SO_4$; and $K,Zn\|Cl,SO_4$, in which an increase in the atomic number and the ionic radius of the alkali metals have a pronounced effect upon the formation of coordination compounds in lateral binary systems, and more especially. upon the formation of hetero compounds within reciprocal systems.

EXPERIMENTAL

Experimental procedure. The present research has involved considerable experimental difficulty, due to the hygroscopicity of lithium chloride and, especially, of zinc chloride; the latter hydrolizes rather easily. In preparing zinc chloride, dehydrating it, and using it in that portion of the system that is rich in $ZnCl_2$, we employed the procedure described in the paper by I. N. Nikonova, S. P. Pavlenko, and A. G. Bergman [6]. The lithium salts and the zinc sulfate ("pure for analysis" brands) used in our research were recrystallized twice.

The fusibility of the system was investigated visually by the polythermal method in a Pyrex test tube.

All compositions are stated in molecular per cent, the double molecules $LiCl_2$ being produced. To save space not all the experimental data are given in this paper.

Binary Systems

1. The $Li_2Cl_2 - Li_2SO_4$ system has been investigated by M. A. Klochko [7] and by O. S. Dombrovskaya [8] Both authors state that this is a system possessing a eutectic, but complicated by the presence of a polymorphic transformation of lithium sulfate at 572°.

The third modification described by Wyrouboff [9] as existing below 500° has not been discovered by subsequent researchers [10,11,12,13,14].

E. I. Banashek has found another break on the LiCl crystallization curve, at 563°, which A. G. Bergman thinks is a hitherto unknown homeomorphic transformation; this transformation is not visible on the differential heating curve of pure LiCl.

We have confirmed these results (Fig. 1 and Table 1). The eutectic point is located at 480° at 46% Li_2Cl_2. A break is seen on the LiCl crystallization curve at 570° and 85%. We made no investigation of the nature of this phenomenon, adopting the purely conventional designations of LiCl α-and β for the respective branches of the LiCl crystallization curve.

2. The $Li_2SO_4 - ZnSO_4$ system (Fig.1,Table 2) has been investigated by N. P. Luzhnaya and I. P. Vereshchetina. The eutectic point is located at 510° and 48.5%

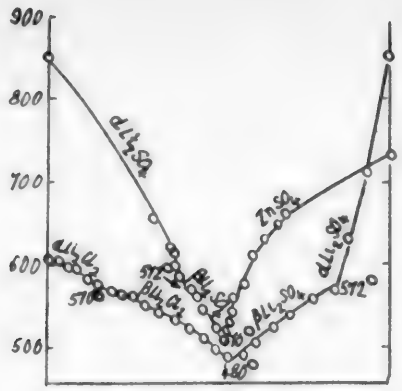

Fig. 1. Fusibility diagram of the Li_2Cl_2 – Li_2SO_4. Fusibility diagram of the Li_2SO_4– $ZnSO_4$.

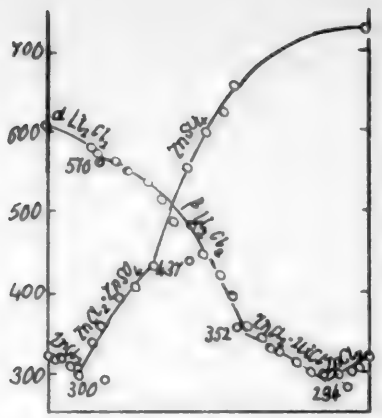

Fig. 2. Fusibility diagram of the Li_2Cl_2 – $ZnCl_2$. Fusibility diagram of the $ZnCl_2$ – $ZnSO_4$.

TABLE 1

Li_2Cl_2 – Li_2SO_4 System

Mol. % Li_2SO_4	t°	Solid phases
0	605	
5.1	596	
8.0	592	α-LiCl
11.6	584	
14.9	572	α-LiCl + β-LiCl
17.9	566	
20.8	563	
24.7	560	
28.2	550	
31.4	542	β-LiCl
34.3	538	
42.1	523	
48.9	596	
52.8	486	
54.0	480	β-LiCl + β-Li_2SO_4
56.8	490	
66.2	522	
71.0	540	β-Li_2SO_4
77.5	556	
83.9	570	
85.0	572	β-Li_2SO_4 + α-Li_2SO_4
88.6	630	α-Li_2SO_4
93.5	710	

TABLE 2

Li_2SO_4 – $ZnSO_4$ System

Mol. % $ZnSO_4$	t°	Solid phases
0	850	
	654	
35.5	618	
36.7	610	α-Li_2SO_4
37.5	600	
39.0	581	
39.5	572	α-Li_2SO_4 + β-Li_2SO_4
42.0	566	
43.5	562	
45.5	548	β-Li_2SO_4
49.5	520	
51.5	510	β-Li_2SO_4 + $ZnSO_4$
52.0	520	
53.0	530	
54.0	542	
55.0	556	
57.3	576	$ZnSO_4$
60.5	612	
63.3	626	
67.5	647	
70.0	657	

Li_2SO_4. The transition point from the α-modification of Li_2SO_4 to the β is located at 572° at 61%. We have confirmed these findings.

3. <u>The Li_2Cl_2 – $ZnCl_2$ system</u> (Fig. 2, Table 3) has been investigated for

TABLE 3

Li_2Cl_2 - $ZnCl_2$ system

Mol. % Li_2Cl_2	t°	Solid phases
0	320	$ZnCl_2$
3.4	302	
6.0	308	
8.8	303	
13.0	294	$ZnCl_2$+$ZnCl_2$·2LiCl
14.8	296	$ZnCl_2$·2LiCl
18.9	306	
23.1	316	
28.1	330	
31.1	335	
34.5	344	
38.5	352	$ZnCl_2$·2LiCl+β-LiCl
38.6	360	β-LiCl
43.2	396	
46.9	425	
51.2	450	
55.7	483	
63.9	517	
69.3	540	
74.4	552	
79.6	562	
82.5	570	β-LiCl+α-LiCl
84.5	576	α-LiCl
86.1	584	

TABLE 4

$ZnCl_2$ - $ZnSO_4$ system

Mol. % $ZnSO_4$	t°	Solid phases
0	322	$ZnCl_2$
2.6	320	
4.8	318	
7.0	310	
9.6	300	$ZnCl_2$+$ZnCl_2$·$ZnSO_4$
13.8	340	$ZnCl_2$·$ZnSO_4$
17.6	356	
22.7	322	
27.2	410	
32.5	436	$ZnCl_2$·$ZnSO_4$+$ZnSO_4$
38.0	490	$ZnSO_4$
43.6	556	
49.0	600	
54.0	627	
59.0	658	

Heat of formation of the salts [17]:

$Li_2Cl_2 + ZnSO_4 \longrightarrow Li_2SO_4 + ZnCl_2$

195.3 + 233.45 340.23 + 99.28

428.75 439.51

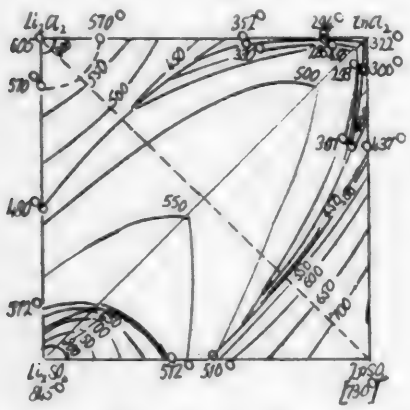

Fig. 3. Projection of the reciprocal system $Li,Zn \| Cl,SO_4$ upon the composition square.

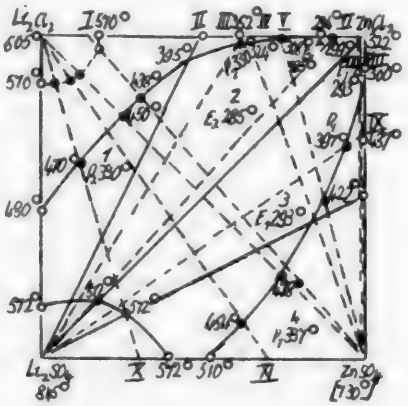

Fig 4. Diagram showing the directions of the internal sections and the triangulation of the reciprocal salt-pair system's square.

the first time by the present authors. There is a break on the crystallization curve at 570° and 82.5%, similar to the one we found in the Li_2Cl_2-Li_2SO_4 system. At 352° and 38.5% Li_2Cl_2 a branch of the curve meets a branch of the binary compound, the composition of which most likely is $ZnCl_2$·2LiCl, analogous to the compound $ZnCl_2$-2NaCl. The binary compound has a eutectic at 294° and

13% Li_2Cl_2.

4. $ZnCl_2$-$ZnSO_4$ system (Fig. 2, Table 4). We are the first to have made a study of this system, which forms the double salt $ZnCl_2.ZnSO_4$. We have adopted this formula for the compound on the basis of thermographic data that will be reproduced in our next paper.

The short crystallization curve for $ZnCl_2$ intersects the $ZnCl_2$-$ZnSO_4$ curve at the eutectic point: 300° and 90% $ZnCl_2$. The incongruent melting point of this double salt is 437°, the transition point being located at 69% $ZnCl_2$.

The Tertiary Reciprocal Salt-Pair System Li,Zn||Cl,SO_4

The shape of the liquidus surface of this system classes it as a typical irreversible reciprocal salt-pair system, which conforms with the nominal thermal effect of the exchange reaction. The heat evolved when the Li_2SO_4 + $ZnCl_2$ pair is formed totals 10.76 Cal, or 5.38 Cal per equivalent.

A general view of this reciprocal salt-pair system and its isotherms is given in Fig. 3 as a projection upon the composition square.

The liquidus surface of the system comprises 7 crystallization areas, plotted from the results obtained along two diagonals and 11 internal sections.

The plan of these sections (fig. 4) indicates the lines along which the system has been investigated.

Diagonal Sections of the System.

1. The stable diagonal Li_2SO_4-$ZnCl_2$ (Fig. 5, Table 5) is a system with a simple eutectic. Its fusibility curve has three crystallization branches: α-and-β-Li_2SO_4, and $ZnCl_2$; the α-and-β-Li_2SO_4 branches meet at 570° and 17% $ZnCl_2$, with the Li_2SO_4 occupying 99% of the diagram. The central section of the Li_2SO_4 branch, which is rather flat, is evidence of the presence of a tendency for the system's components to layer in the liquid state. Curves of similar shape are found in the AgCl-$CdSO_4$ [15] and AgBr-Tl_2SO_4 [16] systems. The eutetic point is located at 310° and 1% Li_2SO_4.

2. The diagonal section $ZnSO_4$-Li_2Cl_2 (Table 6) is more complicated, as it intersects the region of the exchange product Li_2SO_4, in addition to the component regions. There are two points in the system where three curves meet: at 450° and 75% Li_2Cl_2 and at 428° and 26% Li_2Cl_2. The fusibility curve of the exchange product Li_2SO_4 has a maximum at 544°.

TABLE 5a

Details of the Li_2SO_4-$ZnCl_2$ diagonal.

Mol. % Li_2SO_4	t°	Solid phases.
0	522	$ZnCl_2$
0.12	521	
0.3	520	
0.73	318	
1.0	310	$ZnCl_2$β-Li_2SO_4
1.15	340	β-Li_2SO_4
2.0	386	

The diagramsof the internal sections of the Li,Zn||Cl,SO_4 are reproduced in Figs. 6, 7 and 8, the corresponding numerical data being listed in Tables 7, 8 and 9. In view of the fact that the areas of zinc chloride and of the binary compounds are extremely small, part of the sections showing these compounds are reproduced on an enlarged scale. Most of the system's crystallization surface is occupied by the Li_2SO_4 area, totaling 70.24% of the total area of the square (8.9% being α-Li_2SO_4 and 61.34% being β-Li_2SO_4), while the $ZnCl_2$ area totals only 0.21%. Hence, the areas of the two stable components

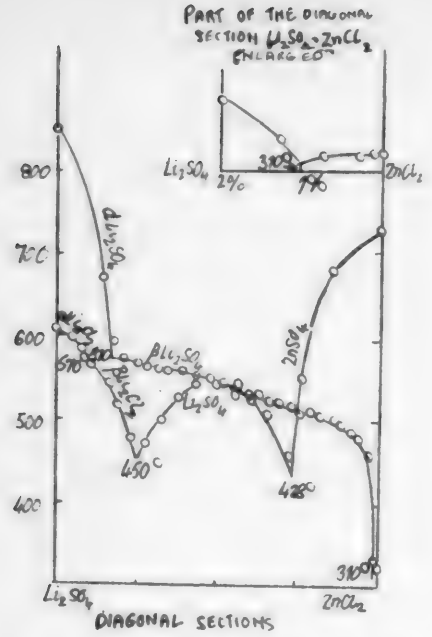

Fig. 5. Fusibility diagram of the diagonal section Li_2SO_4-$ZnCl_2$. Fusibility diagram of the diagonal section $ZnSO_4$-Li_2Cl_2.

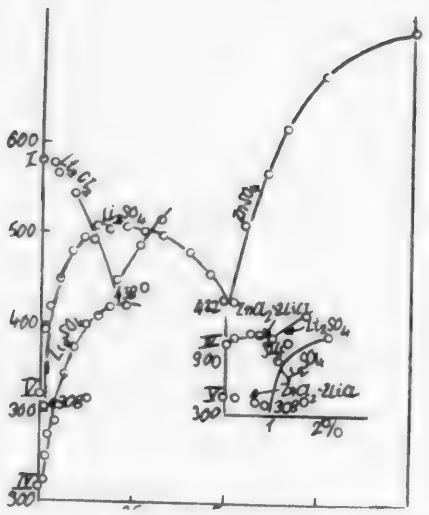

Fig. 6. Fusibility diagrams of the internal sections I, IV, and V of the reciprocal salt-pair system.

TABLE 5

Li_2SO_4-$ZnCl_2$ Diagonal

Mol. % Li_2SO_4	t°	Solid phases.
0	322	$ZnCl_2$
1.0	310	$ZnCl_2$+β-Li_2SO_4
1.5	330	
3.4	437	
6.4	476	
9.3	486	
12.1	496	
14.7	500	
18.3	504	
24.6	510	
30.9	520	β-Li_2SO_4
36.9	526	
44.2	534	
50.8	544	
57.2	552	
65.1	560	
71.0	564	
79.0	570	β-Li_2SO_4+α-Li_2SO_4
82.5	570	
82.6	590	α-Li_2SO_4
85.2	668	

TABLE 6

Li_2Cl_2-$ZnSO_4$ Diagonal

Mol. % $ZnSO_4$	t°	Solid phases
0	605	
4.9	596	α-LiCl
7.9	584	
11.5	570	α-LiCl+β-LiCl
12.5	565	
15.9	540	β-LiCl
19.4	515	
23.6	474	
25.0	450	β-LiCl+β-Li_2SO_4
28.4	468	
33.3	498	
38.3	524	
43.1	544	
47.7	546	β-Li_2SO_4
52.1	544	
56.4	540	
60.8	524	
65.2	504	
72.3	546	
74.0	428	β-Li_2SO_4+$ZnSO_4$
75.7	550	$ZnSO_4$
85.5	680	

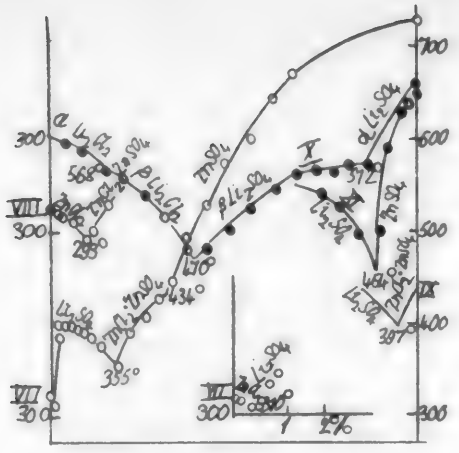

Fig. 7. Fusibility diagrams of the internal sections VII, VIII, IX, X, and XI.

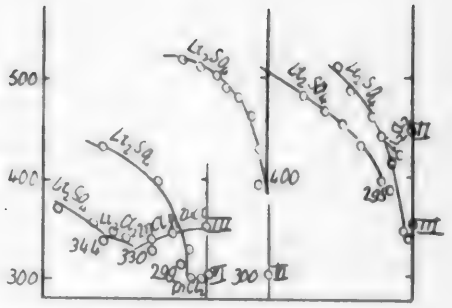

Fig. 8. Fusibility diagrams of the internal sections II, III, and VI.

cover 70.43% of the total area. This is an indication of the degree of irreversibility of the exchange reaction in this system The $ZnSO_4$ area accounts for 14 55%. LiCl accounting for 13 76%, the compound $ZnCl_2.ZnSO_4$ accounting for 0.48%, and the compound $ZnCl_2.2LiCl$ accounting for 0.35%.

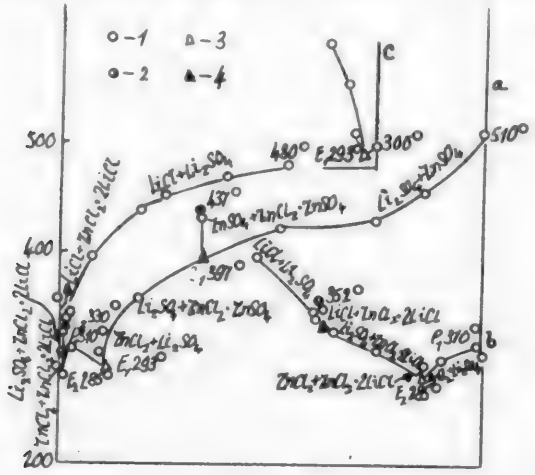

Fig. 9. a) Projection of the joint crystallization line upon the Li_2Cl_2–Li_2SO_4 side of the Li, Zn‖Cl, SO_4 system. b) Part of the projection of the joint crystallization line upon the Li_2Cl_2–$ZnCl_2$ side. c) Part of the projection of the joint crystallization line upon the Li_2Cl_2–$ZnCl_2$ side. 1 - Binary eutectic points; 2 - binary transition points; 3 - ternary eutectic points; 4 - ternary transition points.

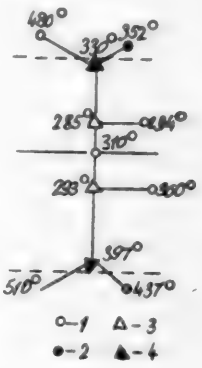

Fig. 10. Diagram of the crystallization tree of the ternary reciprocal salt-pair system Li, Zn‖Cl, SO_4. 1 - Binary eutectic points; 2 - binary transition points; 3 - ternary eutectic points; 4 - ternary transition points-secants.

TABLE 7

Sections: VII 1.5% Li_2Cl_2 +98.5% $ZnCl_2$ ⟶ $ZnSO_4$,
VIII 0.7% Li_2Cl_2 +99.3% $ZnCl_2$ ⟶ $ZnSO_4$,
IX 70% $ZnCl_2$ + 30% $ZnSO_4$ ⟶ Li_2SO_4,
X 70% Li_2SO_4 + 30% $ZnSO_4$ ⟶ Li_2Cl_2,
XI 30% Li_2SO_4 + 70% $ZnSO_4$ ⟶ Li_2Cl_2

Mol. % $ZnSO_4$	t°	Solid phases
Sections VII		
0	318	$ZnCl_2$
0.2	316	
0.4	313	
0.5	310	$ZnCl_2$+β-Li_2SO_4
0.6	316	β-Li_2SO_4
0.8	335	
0.9	347	
2.0	386	
3.0	400	
4.1	400	
5.7	400	
7.5	396	
11.0	386	
14.1	376	
18.4	355	β-Li_2SO_4+ +$ZnCl_2 \cdot ZnSO_4$
22.2	392	$ZnCl_2 \cdot ZnSO_4$
29.1	428	
33.2	434	$ZnCl_2 \cdot ZnSO_4$+ + $ZnSO_4$
33.2	448	$ZnSO_4$
37.3	488	
42.5	530	
54.8	606	
66.2	670	

Mol. % $ZnSO_4$	t°	Solid phases
Sections VIII		
0	322	$ZnCl_2$
1.3	320	
3.0	316	
5.8	312	
9.8	293	$ZnCl_2$+ +$ZnCl_2 \cdot ZnSO_4$
11.6	304	$ZnCl_2 \cdot ZnSO_4$
15.7	330	
Sections IX		
0	436	$ZnCl_2 \cdot ZnSO_4$
1.2	432	
2.5	425	
3.7	416	
4.8	406	
5.0	397	$ZnCl_2 \cdot ZnSO_4$+ +β-Li_2SO_4
[illegible]	401	β-Li_2SO_4
7.7	[illegible]	
9.3	416	
10.9	425	
Sections X		
0	606	α-LiCl
4.3	599	
8.2	590	
11.9	580	
15.2	568	α-LiCl+ +β-LiCl

Mol. % Li_2Cl_2	t°	Solid phases
Sections X		
19.8	558	β-LiCl
25.2	540	
31.0	516	
36.9	484	
39.5	470	β-LiCl+ +β-Li_2SO_4
42.6	482	β-Li_2SO_4
48.6	504	
54.8	526	
61.2	548	
67.2	564	
72.6	566	
77.4	568	
81.5	572	
86.0	575	α-Li_2SO_4+ +β-Li_2SO_4
86.8	576	β-Li_2SO_4
Sections XI		
0	648	$ZnSO_4$
2.5	640	
4.1	632	
7.9	592	
10.0	500	
11.5	454	$ZnSO_4$+ +β-Li_2SO_4
15.4	498	β-Li_2SO_4
20.9	526	
25.9	540	
30.9	548	

In the Li_2SO_4 area the isotherms are prolonged in the direction of the stable diagonal, their curvature being extremely high where they cross it below 500°, these crossings approaching the shape of the meeting of separate curves, so that the isotherms acquire a singular character. The isotherms cross the stable diagonal more smoothly as the temperature is raised, which is evidence that the reaction is somewhat reversible.

The curves of joint crystallization meet at four nonvariant points; the temperature and the composition of the phases in equilibrium are listed in Table 10.

The stable diagonal Li_2SO_4-$ZnCl_2$ divides the square of the reciprocal

TABLE 8

Sections:

I 85% Li_2Cl_2 + 15% $ZnCl_2$ → $ZnSO_4$
IV 35% Li_2Cl_2 + 65% $ZnCl_2$ → $ZnSO_4$
V 25% Li_2Cl_2 + 75% $ZnCl_2$ → $ZnSO_4$

Mol. % $ZnSO_4$	t°	Solid phases
Section I		
0	580	α-LiCl
2.5	578	
4.0	570	α-LiCl+β-LiCl
9.0	544	β-LiCl
14.5	493	
20.0	438	β-LiCl+β-Li_2SO_4
20.3	446	β-Li_2SO_4
26.2	486	β-Li_2SO_4
31.8	515	
Section IV		
0	320	$ZnCl_2$·2LiCl
0.18	322	
0.45	328	
0.72	328	
1.0	324	$ZnCl_2$·2LiCl+β-Li_2SO_4
1.7	350	β-Li_2SO_4
2.6	370	
4.3	390	
6.8	443	
9.1	472	
12.7	496	
15.4	506	β-Li_2SO_4
19.1	518	
23.1	518	

Mol. % $ZnSO_4$	t°	Solid phases
Section V		
0	320	$ZnCl_2$·2LiCl
0.2	318	
0.6	316	
0.9	313	
1.0	308	$ZnCl_2$·2LiCl+β-Li_2SO_4
1.2	358	β-Li_2SO_4
2.2	390	
3.3	416	
5.4	448	
8.4	478	
11.2	495	
15.5	504	
18.7	506	
23.1	506	
27.5	503	
33.1	498	
40.0	478	
45.6	456	
50.9	422	β-Li_2SO_4+$ZnSO_4$
55.9	506	$ZnSO_4$
60.8	568	
65.9	616	
75.7	677	

salt-pair system into two primary ternary systems: Li_2SO_4-Li_2Cl_2-$ZnCl_2$ and $ZnCl_2$-Li_2SO_4-$ZnSO_4$.

Inasmuch as there are binary compounds on the $LiCl_2$-$ZnCl_2$ and $ZnCl_2$-$ZnSO_4$ sides of the square, each of the two foregoing triangles may be divided in turn into two subordinate triangles.

The triangulation of the square is shown in Fig. 4.

In Fig. 9, a, b, and c are projections of the joint crystallization curves upon the sides of the square, while Fig. 10 is a sketch of the crystallization tree, plotted from the triangulation data.

In all the systems we have studied that contain a zinc salt we find a rather marked trend toward the formation of compounds, there are 7 areas in the diagram of the NaCl-KCl-$ZnCl_2$ system, NaCl-KCl forming continuous solid solutions that decompose in the ternary system. The diagram of the Na, Zn‖Cl,SO_4 system exhibits 10 areas, the K, Zn‖Cl,SO_4 system having 16 areas, and the Li,Zn‖Cl, SO_4 system having only 6. This may be explained by the fact that the two factors controlling the exchange reaction and the formation of a co-ordination compound,

TABLE 9

Sections:

II-50% Li_2Cl_2 + 50% $ZnCl \longrightarrow Li_2SO_4$
III-37.5% Li_2Cl_2 + 62.5% $ZnCl_2 \longrightarrow Li_2SO_4$,
VI-10% Li_2Cl_2 + 90% $ZnCl_2 \longrightarrow Li_2SO_4$

Mol. % Li_2SO_4	t°	Solid phases.	Mol. % Li_2SO_4	t°	Solid phases
Section II			Section III		
0	444	β-LiCl	2.2	354	
3.7	423	β-LiCl	2.9	374	
7.6	395	β-LiCl+β-Li_2SO_4	5.0	412	
11.9	433		7.2	441	β-Li_2SO_4+β-Li_2SO_4
16.4	452	β-Li_2SO_4	9.5	460	
21.2	468	β-Li_2SO_4	15.0	486	
21.6	482		18.5	506	
Section III			Section VI		
0	350	$ZnCl_2 \cdot 2LiCl$	0	320	$ZnCl_2$
0.7	347	$ZnCl_2 \cdot 2LiCl$	0.2	300	$ZnCl_2$
1.1	338		0.3	299	$ZnCl_2$+β-Li_2SO_4
1.5	330	$ZnCl_2 \cdot 2LiCl$+β-LiCl	0.4	326	
1.6	340	β-LiCl	0.6	358	
1.9	343	β-LiCl	1.0	394	
2.0	344	β-LiCl+β-Li_2SO_4	2.1	398	
			4.1	460	
			7.0	480	β-Li_2SO_4
			9.8	490	
			12.8	502	
			16.3	510	
			20.3	516	

TABLE 10

Points	Nature of point	t	Composition, Mol. %				Phases in equilibrium
			Li_2Cl_2	Li_2SO_4	$ZnCl_2$	$ZnSO_4$	
1	Transition	330	35.5	2.0	62.5	-	LiCl, $ZnCl \cdot 2LiCl$, Li_2SO_4
2	Eutectic	285	13.0	0.5	86.5	-	$ZnCl_2$, $ZnCl_2 \cdot 2LiCl$, Li_2SO_4
3	Eutectic	293	-	0.7	90.3	9.0	$ZnCl_2$, $ZnCl_2 \cdot ZnSO_4$, Li_2SO_4
4	Transition	397	-	5.0	66.3	28.7	$ZnSO_4$, $ZnCl_2 \cdot ZnSO_4$, Li_2SO_4

namely, the magnitude of the nominal thermal effect of the double decomposition reaction and the tendency of the reaction to form the Li_2SO_4-$ZnCl_2$ pair, which does not form a kainite, do not favor the formation of a co-ordination compound in this sytem.

As a rule, a co-ordination compound of the kainite type is formed whenever the salts constituting the kainite, $\overset{I}{MeCl}$ and $\overset{II}{MeSO_4}$ are components of a stable diagonal Otherwise, i e., when they lie on an unstable diagonal, the effect of the double decomposition reaction will prevail over the forces making for the formation of a co-ordination compound.

In our system, the stable components Li_2SO_4 and $ZnCl_2$ can form the kainite $LiCl \cdot ZnSO_4$ only as the result of the $Li_2SO_4 + ZnCl_2 \longrightarrow 2LiCl + ZnSO_4$ exchange, which requires the expenditure of 10.76 Cal according to the nominal calculation.

Since we know that the thermal effect involved in the formation of double salts is of the order of a few calories (usually not exceeding 10 calories), it is apparent that no co-ordination compound can be formed within the system when the nominal thermal effect of the double decomposition reaction is high enough (5.38 Cal per equivalent).

SUMMARY

1. The binary systems Li_2Cl_2-$ZnCl_2$ and $ZnCl_2$-$ZnSO_4$ and the ternary reciprocal salt-pair system $Li_2Cl_2 + ZnSO_4 \longrightarrow Li_2SO_4 + ZnCl_2$, which is an irreversible reciprocal salt-pair system with an equilibrium shifted toward the $Li_2SO_4 + ZnCl_2$ pair, have been investigated by the visual-polythermal method.

2. The following binary compounds have been revealed: $ZnCl_2.2LiCl$, with an incongruent melting point at 352°, and $ZnCl_2.ZnSO_4$, with an incongruent melting point at 437°.

3. Eight crystallization areas of solid phases have been found in the $Li,Zn \| Cl,SO_4$ system, namely: α- and β-Li_2SO_4, α- and β-LiCl, $ZnCl_2$, $ZnSO_4$, and the two compounds $ZnCl_2.2LiCl$ and $ZnCl_2.ZnSO_4$.

4. The crystallization tree of the system has two ternary eutectic points, two ternary transition points, and one saddle eutectic point on the stable diagonal.

5. The system is characterized by the following features: a) the extremely small size of the area of one of the stable components, $ZnCl_2$ (the eutectic on the stable diagonal is located at 99% $ZnCl_2$), and the tendency to layer in the liquid state in the middle portion of the diagram, which is also indicated by the rather flat shape of the Li_2SO_4 crystallization curve; and b) the absence of a compound of the kainite type that is characteristic of monovalent cations with a large radius in MeX-$ZnSO_4$ systems (where Me^+ is K, Rb, Cs, or Tl, and X is Cl, Br, or I).

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Received October 2, 1949.

POLAROGRAPHIC INVESTIGATION OF SOME ORGANIC ACIDS

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The ability of organic acids to undergo reduction at a dropping mercury electrode was observed by Gerasimenko [1] in the case of oxalic acid. His paper unfortunately gives no information on the magnitude of the diffusion current.

We took no account of the earlier research by Conant [2], which contains reports of the reduction of some organic acids possessing various functional groups within the molecule, because the waves he recorded were due to the double bonds and the NO_2 group contained in the acids tested. In 1936 Winkel and Proske [3] investigated oxalic acid and were the first to measure the magnitude of its diffusion currents. They did not determine the quantitative variation of the i_d with concentration, however.

Down to 1942 all subsequent polarographic research on organic acids dealt with acids whose molecules contained other functional groups or double bonds. More than ten such acids have been investigated by now [4-6]. In 1942 Furman and Bricker [7] investigated phthalic acid, securing two characteristic waves for it.

Winkel and Proske [3] tested other saturated dibasic acids besides oxalic acid, none of them being reduced in the medium employed (0.1 N NH_4Cl). They therefore assumed that the carboxyl groups had to be conjugated to produce waves, though this becomes hardly likely in the light of the above-cited data on phthalic acid.

Thus, the experimental data on the reduction of simple organic acids is extremely sparse. Down to recently, characteristic polarographic waves having been recorded only for oxalic and phthalic acids, and the variation of the i_d with concentration having been determined only for phthalic acid. A large amount of experimental data on the reduction of organic acids at a dropping mercury electrode is contained in a paper by I. A. Korshunov, Z. B. Kuznetsova, and M. K. Shchennikova [9], published in December 1949, in which the authors give figures for the $E_{1/2}$ and the diffusion current for many monobasic acids and their chloro derivatives, as well as for several dicarboxylic acids. Korshunov, Kuznetsova, and Shchennikova have found that the diffusion current is a linear function of the concentration for the acids tested, and they also discovered how the diffusion currents vary with the dissociation constants of these acids. We have investigated several organic acids at the same time that Korshunov, Kuznetsova, and Shchennikova did their research.

In order to secure experimental data on simple organic acids, which we required to be able to judge the influence of molecular structure upon the reduction process, we made a study of several saturated monobasic and dibasic acids, aliphatic as well as aromatic.

Experimental procedure. We used an ordinary electrolyzer in our research

which was fitted with equipment to blow hydrogen through the solution, a funnel to determine the weight of a drop, and a device to measure the potential at the bottom of the vessel.

In our polarography we used a capillary with $\underline{m}$ = 0.582 mg/sec and $\underline{t}$ = 4.8 sec and another with $\underline{m}$ = 0.428 mg/sec and $\underline{t}$ = 3.5 sec. The bottom potential was measured periodically against a saturated electrode; it was found to be +0.333 volt referred to the standard hydrogen electrode. All our research was carried out at 15° C. For Table see Plate, p. 2137.

The following acids were reduced: formic, benzoic, salicylic, oxalic, malonic, and phthalic, plus mixtures of one acid with another.

The formic acid had a concentration of $1.93 \cdot 10^{-3}$ mol/liter, while the concentration of the benzoic acid ranged from $3.09 \cdot 10^{-3}$ to $1.5 \cdot 10^{-2}$ mol/liter, that of the salicylic acid ranged from $2 \cdot 10^{-3}$ to $1.3 \cdot 10^{-2}$ mol/liter, that of the oxalic from $1 \cdot 10^{-3}$ to $5 \cdot 10^{-3}$ mol/liter, that of the malonic from $1 \cdot 10^{-3}$ to $8 \cdot 10^{-3}$ mol/liter, that of the lactic from $3 \cdot 10^{-3}$ to $7 \cdot 10^{-3}$ mol/liter, that of the glycolic from $1 \cdot 10^{-3}$ to $6 \cdot 10^{-3}$ mol/liter, and that of the phthalic from $3 \cdot 10^{-3}$ to $3.5 \cdot 10^{-3}$ mol/liter.

0.1 N KCl was used as the electrolyte medium.

Polarography was done with the M-7 visual polarograph and the M-3 mirror galvanometer of the Chemistry Research Institute of Gorky State University.

The value of $E_{1/2}$ was determined graphically by two methods:

1) The potential equivalent to half the diffusion current was found.
2) The potential was found at which $\ln \frac{i}{i_d - i}$ was zero.

In every case the values of $E_{1/2}$ and E given in the polarograms are referred to the standard hydrogen electrode. The $E_{1/2}$ values have been corrected for the iR drop.

EXPERIMENTAL

Formic acid. We have found that one wave with an $E_{1/2}$ = -1.38 volt is produced when formic acid of $1.98 \cdot 10^{-3}$ mol/liter concentration is reduced at a dropping mercury electrode

We have found that the diffusion current is a linear function of the formic acid concentration.

Benzoic acid. We have found that the reduction of benzoic acid results in the formation of one polarographic wave with an $E_{1/2}$ = -1.36 volt (see Fig. 1).

Changing the concentration for $3.5 \cdot 10^{-3}$ to $1.5 \cdot 10^{-2}$ mol/liter produces no shift in the value of $E_{1/2}$.

We have found a function expressing the variation of the diffusion current with acid concentration in this concentration range:

$$i_d = k\ 0.52\ c,$$

where i_d is the diffusion current, in microamperes, $\underline{k}$ is a proportionality factory, and $\underline{c}$ is the concentration, in millimols per liter.

We have found that for benzoic acid $\underline{k}$ = 3.51, while $0.52 = 605 \cdot m^{2/3}\ t^{1/6}\ D^{1/2}\ \alpha,$ [1] where 605 is the coefficient in the Ilkovich equation, $\underline{m}$ is the quantity

1) α is a coefficient replacing $\underline{n}$ in the wave equation:

$$E = E_{1/2} + \frac{RT}{nF} \ln \frac{i}{i_d - i}$$

for irreversible reduction.

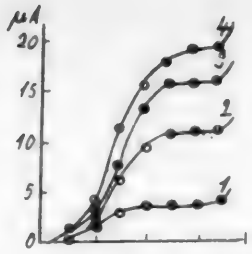

Fig. 1. Polarograms of benzoic acid.

Curves: 1 - concentration of $3.09 \cdot 10^{-3}$ mol/liter; 2 - $5.15 \cdot 10^{-3}$ mol/liter; 3 - $7.91 \cdot 10^{-3}$ mol/liter; 4 - $1.07 \cdot 10^{-2}$ mol/liter.

Origin of curves at -1.07 volt.

Verticals spaced 0.2 volt apart.

of mercury flowing out of the capillary, in mg per sec, t is the dropping period, in seconds, and D is the diffusion coefficient of the reduced or oxidized substance, in cm^2 per sec.

This equation is the Ilkovich equation with the coefficient 3.51 inserted on the basis of the experimental data. More will be said about this below.

We determined the coefficient α from the slope of the straight line $E - \log \frac{i}{i_d - i}$ it being 0.46 for benzoic acid.

The diffusion coefficient was calculated in every case from the Stokes-Einstein equation:

$$D = \frac{RT}{k} \frac{(4\pi kd)^{1/3}}{6\pi\eta(3M)^{1/3}},$$

where D is the diffusion coefficient, in sq cm/deg, R is the gas constant, in ergs per degree, T is the Kelvin temperature, K is Avogardo's number, M is the molecular weight, d is the density of the substance in the solid state, and η is the coefficient of viscosity of the solution, in dynes per sq cm per sec.

Friedman and Carpenter [8] determined the limits within which this equation was accurate in terms of the molecular volume (molecular weight: density) when η is taken as the coefficient of viscosity of water; they found that it holds good at infinite dilution for substances whose molecular weight does not exceed 180. It was thus possible to employ it in that form for polarographic measurements when low concentrations were used.

The diffusion coefficient of benzoic acid was found to be $0.723 \cdot 10^{-5}$ sq cm per sec.

Salicylic acid. The reduction of salicylic acid involves the formation of one polarographic wave with an $E_{1/2}$ of -1.29 volt (Fig. 2). As was the case with benzoic acid, changes in concentration over the tested range, i.e., from $2\ 10^{-3}$ to $1.3 \cdot 10^{-2}$ mol/liter, produced no change in the value of $E_{1/2}$. We found that the diffusion current was a linear function of concentration:

$$i_d = k\ 0.50c.$$

We found that for salicylic acid $k = 4.75$, $0.50 = 605\ m^{2/3}t^{1/6}D^{1/2}\alpha$; $D = 0.726 \cdot 10^{-5}$ sq cm per sec, and (n) $\alpha = 0.44$.

Thus we found that the quantitative variation of i_d with concentration is expressed by the Ilkovich equation for formic, benzoic, and salicylic acids, with the coefficient k inserted on the basis of our experimental data.

Glycolic acid. The polarogram of glycolic acid exhibits one wave with an $E_{1/2}$ of 1.32 volt (Fig. 3), changes in the acid concentration not causing any shift in the $E_{1/2}$.

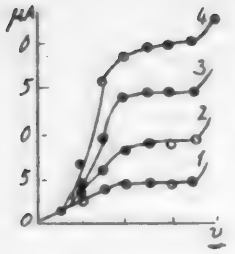

Fig. 2. Polarograms of salicylic acid.

Curves: 1- concentration of $2.0 \cdot 10^{-3}$ mol/liter; 2 - $3.92 \cdot 10^{-3}$ mol/liter; 3 - $6.3 \cdot 10^{-3}$ mol/liter; 4 - $7.73 \cdot 10^{-3}$ mol/liter.

Origin of curves at -1.07 volt.

Verticals spaced 0.2 volt apart.

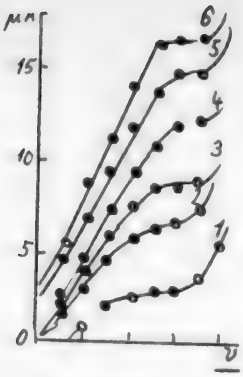

Fig. 3. Polarograms of glycolic acid.

Curves: 1 - concentration of $1 \cdot 10^{-3}$ mol/liter; 2 - $2 \cdot 10^{-3}$ mol/liter; 3 - $3 \cdot 10^{-3}$ mol/liter; 4 - $4 \cdot 10^{-3}$ mol/liter; 5 - $5 \cdot 10^{-3}$ mol/liter; 6 - $6 \cdot 10^{-3}$ mol/liter.

Origin of curves at -1.07 volt.

Verticals spaced 0.2 volt apart.

We found the variation of the diffusion current to be the following function of the concentration of glycolic acid:

$$i_d = k\ 0.275\ c,$$

where i_d is the diffusion current, in microamperes, k is a proportionality factor, and c is the concentration of glycolic acid, in millimols per liter.

We found that in the case of glycolic acid $k = 0.09$; $0.275 = 605 \cdot m^{2/3} \cdot t^{1/6} \cdot D^{1/2} \cdot \alpha$, where $(n)\alpha = 0.20$; and $D = 0.726 \cdot 10^{-5}$ sq cm per sec.

Lactic acid. We have found that there is only one wave, with an $E_{1/2}$ of -1.37 volt (Fig. 4) in the polarograms of lactic acid, while changes in the lactic acid concentration cause no shift in the $E_{1/2}$ within the concentration range explored.

We found the following equation to govern the variation of the diffusion current with the concentration of lactic acid:

$$i_d = k\ 0.448\ c.$$

For lactic acid, k was found to equal 0.241; $D = 0.797 \cdot 10^{-5}$ sq cm per sec; $(n)\alpha = 0.33$; $0.448 = 605 \cdot m^{2/3} t^{1/6} D^{1/2} \alpha$.

Oxalic acid. The polarogram of oxalic acid exhibits one wave with an $E_{1/2}$ of -1.31 volt (Fig. 5). Changes in the oxalic acid concentration from $1 \cdot 10^{-3}$ to $4 \cdot 10^{-3}$ mol/liter caused no shift in the $E_{1/2}$.

The variation of the diffusion current with concentration is given by the equation:

$$i_d = k\ 0.4\ c.$$

The diffusion coefficient for oxalic acid is $0.783 \cdot 10^{-5}$ sq cm per sec; $(n)\alpha$ = 0.27; and k = 10.1.

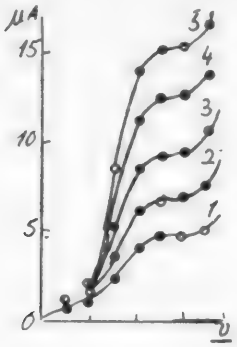

Fig. 4. Polarograms of lactic acid.

Curves: 1 - concentration of $3 \cdot 10^{-3}$ mol/liter; 2 - $4 \cdot 10^{-3}$ mol/liter; 3 - $5 \cdot 10^{-3}$ mol/liter; 4 - $6 \cdot 10^{-3}$ mol/liter; 5 - $7 \cdot 10^{-3}$ mol/liter.

Origin of curves at -1.07 volt.

Verticals spaced 0.2 volt apart.

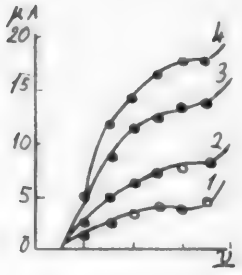

Fig. 5. Polarograms of oxalic acid.

Curves: 1 - concentration of $1 \cdot 10^{-3}$ mol/liter; 2 - $2 \cdot 10^{-3}$ mol/liter; 3 - $3 \cdot 10^{-3}$ mol/liter; 4 - $4 \cdot 10^{-3}$ mol/liter.

Origin of curves at -1.07 volt.

Verticals spaced 0.2 volt apart.

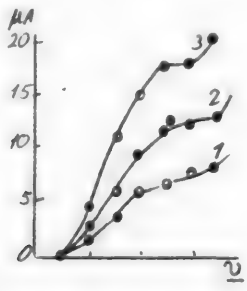

Fig. 6. Polarograms of malonic acid.

Curves: 1 - concentration of $3 \cdot 10^{-3}$ mol/liter; 2 - $5 \cdot 10^{-3}$ mol/liter; 3 - $8 \cdot 10^{-3}$ mol/liter.

Origin of curves at -1.07 volt.

Verticals spaced 0.2 volt apart.

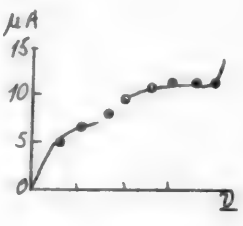

Fig. 7. Polarograms of phthalic acid.

Concentration $3 \cdot 10^{-3}$ mol/liter.

Origin of curve at -0.97 volt.

Verticals spaced 0.2 volt apart.

Malonic acid. We have found that one polarographic wave is formed, with an $E_{1/2}$ of -1.34 volt (Fig. 6), when malonic acid is reduced. Changes in the concentration of malonic acid from $2 \cdot 10^{-3}$ to $8 \cdot 10^{-3}$ mol/liter cause no shift in the $E_{1/2}$.

The variation of the diffusion current with concentration is given by the following equation:

$$i_d = 0.48 kc.$$

We found the following values for malonic acid: $k = 4.96$; $D = 0.783 \cdot 10^{-5}$ sq cm per sec; $(n)\alpha = 0.32$; and $0.48 = 6.05 \cdot m^{2/3} t^{1/6} D^{1/2} \alpha$.

Phthalic acid. The reduction of phthalic acid is accompanied by two polarographic waves. The first wave has an $E_{1/2}$ of -1.0 volt, and the second an $E_{1/2}$ of -1.29 volt (Fig. 7).

With the exception of phthalic acid, the reduction of mixtures of the foregoing acids at a dropping mercury electrode results in the formation of only one polarographic wave in each instance, owing to the slight difference between the values of $E_{1/2}$ for the various acids, the $E_{1/2}$ being usually shifted from the original $E_{1/2}$ values by 0.4 to 0.6 volt to one side or the other. The polarograms of mixtures containing phthalic acid exhibit two waves, the $E_{1/2}$ being the same as that for phthalic acid (Fig. 8).

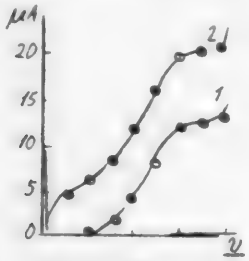

Fig. 8. Polarograms of a mixture of benzoic and phthalic acids.

Curves: 1 - benzoic acid; 2 - benzoic + phthalic acids.

Origin of curves at -0.97 volt.

Verticals spaced 0.2 volt apart.

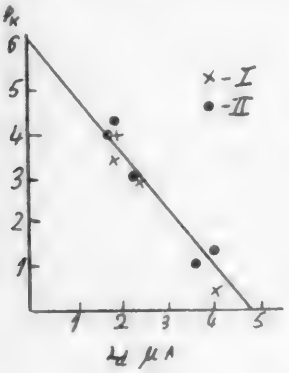

Fig. 9. Variation of the first dissociation constant with the diffusion current constant for salicylic and malonic acids when the electrolytic medium is 0.1 N KCl. I - Salicylic acid; II - malonic acid.

The relationship between the first dissociation constant and the diffusion current constant derived by Korshunov, Kuznetsova, and Shchennikova [9] for several monobasic acids as well as for some dicarboxylic acids when the electrolytic medium was LiCl or $(CH_3)_4I$ has the same form for the acids we have tested in a KCl solution:

$$\frac{i_d}{c} = a - bp_k,$$

the sole difference being that when KCl is used as the electrolytic medium, the coefficients $a = 4.40$ and $b = 0.53$ (Fig. 9).

SUMMARY

1. The halfwave potentials of formic, benzoic, salicylic, glycolic, lactic, oxalic, and phthalic acids have been measured at various concentrations in a given electrolytic medium.

2. It has been found that the value of $E_{1/2}$ does not depend upon the concentration in any of these acids.

3. The values of the coefficient α have been determined, and $\log \frac{i}{i_d - i}$ has been found to be a linear function of E.

4. The way in which the magnitude of the diffusion currents vary with acid concentration has been established.

5 The halfwave potentials of the monobasic acids – formic and benzoic – are more negative than those of oxalic, malonic, and phthalic acids.

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Received December 20, 1949.

POLAROGRAPHIC INVESTIGATION OF SOME KETONES

M. I. Bobrova and P. N. Sokolov

The number of ketones investigated polarographically by various authors is fairly high, exceeding 30. Only for 18 of them has the halfwave potential been determined. And of these 18, only 9 are simple monoketones whose molecules contain no other functional groups [2, 3, 4, 5].

The halfwave potential is an important polarographic characteristic of a compound, and the first thing we have to know in order to reach any conclusion regarding the electrolytic reduction of compounds of this class is the halfwave potential for as many of these compounds as possible. This has been the objective of the present research: determining the major polarographic chacteristics of some of the ketones investigated previously.

Polarography was performed with the M-7 visual polarograph and the M-3 mirror galvanometer of the Chemistry Research Institute of Gorky State University. The usual vessel was employed as the electrolyzer, fitted with a tube to blow hydrogen through the solution, a funnel to determine the weight of drops, and a device for measuring the potential at the bottom of the vessel. A capillary with $\underline{m}$ = 0.60 mg/sec and $\underline{t}$ = 4.8 sec was used in all the tests. All our research was carried out at 15°.

Substances: the chloromethyl ethyl ketone and α-chloroethyl methyl ketone were furnished us by the A. E. Favorsky Laboratory of Leningrad State University, where they had been synthesized by S. N. Danilov and N. S. Tikhomirova [1]. All the other ketones were Kahlbaum preparations of the 'for analysis' grade.

The indifferent electrolyte employed throughout was a solution of 0.01N HCl and 0.01N KCl in 80% (by volume) C_2H_5OH. The pH of this mixture was 3.3, measured with a quinhydrone electrode. The values of $E_{1/2}$ and E are given throughout referred to the standard hydrogen electrode.

The potential at the bottom of the vessel was measured periodically against a saturated calomel electrode. It remained constant throughout the tests at +0.29 volt.

Benzophenone. Benzophenone had been investigated earlier [2, 3, 4, 6, 7]; we used it to compare our results with the figures given in the literature.

Pasternak [2] cites the following results (Table 1).

TABLE 1

Reduction of Benzophenone (Pasternak)

pH	1.3	4.9	7.2	8.6	11.3
$E_{1/2}$(V), referred to a standard calomel electrode	-0.94	-1.16	-1.29	-1.36	-1.42
α[1]	1.15	1.75	—	1.90	—
Reduction product	Benzopinacol	Benzopinacol + Benzohydrol	—	Benzohydrol	—

[1]) α is a coefficient that takes the place of the coefficient $\underline{n}$ in the wave equation $E = E_{1/2} + \frac{RT}{nF} \lg \frac{i}{i_d - i}$ when reduction is irreversible.

His halfwave potentials lie on a straight line when plotted against the pH. Interpolating them for pH 7 gives an $E_{1/2}$ of −1.28 volt, which agrees approximately with the values found by Adkins and Cox (−1.25) and by Stromberg and Reinus (−1 24). Interpolating this curve for pH 3.3 yields an $E_{1/2}$ of −1.7 volt; we were interested in comparing the values of $E_{1/2}$ in electrolytic media that differed not only in their pH but also chemically [NH_4Cl, $(CH_3)_4OH$] [1], a Kolthoff buffer [6], a citrate buffer [2], etc.

Our findings were as follows (Table 2 and the figure):

TABLE 2

Reduction of Benzophenone

c, mol/liter	i_d(A)	$E_{1/2}$(V)		α
		referred to a standard hydrogen electrode	referred to a standard calomel electrode	
10^{-3}	$0.33.10^{-5}$	−0.80	−1.08	0.2
	$0.75.10^{-5}$	−1.37	−1.65	0.2

As we see in Table 2, benzophenone is reduced in two stages at pH = 3.3 the $E_{1/2}$ first stage agreeing with the value obtained by interpolation from the Pasternak data.

We employed the usual method to determine α: the wave was plotted in $E - \lg \frac{i}{i_d - i}$ coordinates; this yielded a straight line, the slope of which was set equal to $\frac{2.3RT}{\alpha F}$:

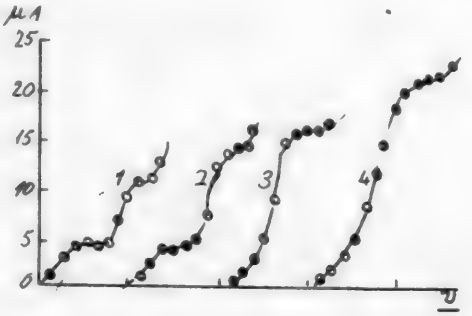
$$\frac{\Delta E}{\Delta \lg \frac{i}{i_d - i}} = \frac{2.3RT}{\alpha E},$$

whence, under our experimental conditions (15°):

$$\alpha = 0.057 \frac{\Delta \lg \frac{i}{i_d - i}}{\alpha E}.$$

The agreement between the values of $E_{1/2}$, is evidence of the similarity in the first stage of the electrode reaction in our experiment and in the reduction of benzophenone by the authors cited [2, 6, 7].

Together with the $E_{1/2}$ the coefficient α is also a highly typical characteristic of electrode reduction. Unfortunately, the value of α is not specified in all of the above-mentioned papers. Even Pasternak's figures differ from ours by a factor of about 6, notwithstanding the similarity of the methods employed to determine α. In view of the agreement between the values of $E_{1/2}$, this discrepancy leads us to believe that there is a difference in the nature of the second – irreversible – stages of benzophenone



Polarograms of the reduction of: 1) benzophenone, 2) paratolyl phenyl ketone, 3) chloromethyl ethyl ketone, and 4) α-chloroethyl methyl ketone, at pH 3.3. Origin of curves: 0.51 volt, referred to the standard hydrogen electrode. Verticals spaced 0.8 volt apart.

reduction in media of different salt composition. Furman and Bricker [8], who found that the coefficient α changed 100% when phthalic acid was reduced in electrolytic media of the same pH but of different composition, thus indicate a similar discrepancy between the values of α in media of different composition.

Paratolyl phenyl ketone. The polarogram of paratolyl phenyl ketone exhibits two characteristic waves, their $E^1/_2$ being [illegible] and 1.41 volts, respectively. In both cases the value of α was 0.2.

Chloromethyl ethyl ketone and α-chloroethyl methyl ketone. Both of these chloro derivatives of ethyl methyl ketone display their own characteristic waves. The values of $E^1/_2$, i_d, and d are given in Table 3.

TABLE 3

Reduction of Chloro Derivatives of Ethyl Methyl Ketone

Substance	c, mol/liter	i_d(A)	$E_{1/2}$(V)	α
Chloromethyl ethyl ketone	$2\cdot10^{-2}$	$1.2\cdot10^{-5}$	−1.21±0.02	0.23
α-chloroethyl methyl ketone	$2\cdot10^{-2}$	$2.5\cdot10^{-5}$	−1.30±0.02	0.23

We see in Table 3 that these two chloro derivatives of ethyl methyl ketone can be identified polarographically in the electrolytic medium employed.

Butyl methyl ketone and dipropyl ketone do not yield any characteristic waves in this medium, i.e., they are not reduced at the cathode. The butyl methyl ketone was also polarographed in media whose pH ranged from 2 to 6 without any waves being found.

SUMMARY

1) The $E^1/_2$ and α have been measured for benzophenone, paratolyl phenyl ketone, chloromethyl ethyl ketone, and α-chloroethyl methyl ketone.

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Received December 20, 1949

THE THERMAL DECOMPOSITION OF THE CALCIUM SALTS OF MONOCHLORO- AND TRICHLOROACETIC ACIDS

M. S. Malinovsky and A. P. Grishchuk

The thermal decomposition of salts of carboxylic acids is widely employed in organic chemistry in the preparation of ketones. A very thorough study has been made of the decomposition of calcium acetate, which decomposes at an appreciable rate at a temperature somewhat higher than 400°, the main decomposition product being acetone, though minute quantities of ethyl methyl ketone and acetic acid are also recovered.

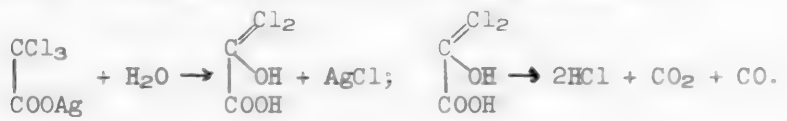
Kanevskaya, Bamdas, and Shemyakin have made a study of the thermal decomposition of the copper and silver salts of the following acids, acetic, benzoic, and opianic acids, to discover the mechanism involved in the pyrogenic decomposition of salts of carboxylic acids; they concluded that decomposition of these acids involves a stage in which a metallic oxide is split out, yielding an acid anhydride as an intermediate product [1, 2, 3, 4]. Bamberger advanced this hypothesis of the possible mechanism involved in the decomposition of acids when their salts were heated as far back as 1910 [6], but he did not support it with any experimental evidence, so that the question remained unsolved until the above-mentioned researches of these Soviet scientists. Continuing their research, Bamdas and Shemyakin later investigated the thermal decomposition of the calcium salts of benzoic and opianic acids [5].

It may be asserted that all these investigations have provided some theoretical underpinning for the thermal decomposition of salts of these acids. Matters are much less satisfactory as far as the thermal decomposition of substituted acids, containing various groups, such as halides, within the acid radical, are concerned. We have undertaken a series of researches in this field to fill this gap, which are the topic of the present report We began with a study of the decomposition of the calcium salts of monochloroacetic and trichloroacetic acids.

Long ago, Engler and Stende [7] made a study of the thermal decomposition of these acids in a sealed tube at 300°. The authors comment on the fact that the cleavage of these acids was not smooth, the trichloroacetic acid decomposing, it seems, as follows:

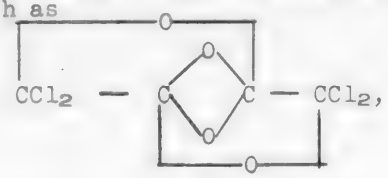
$$2CCl_3COOH \rightarrow CCl_3COCl + CO_2 + CO + 2HCl,$$

as was indicated by analysis of the gaseous reaction products, which consisted of 23.2% carbon dioxide, 25.4% carbon monoxide, and 51.4% hydrogen chloride (all percentages by volume). Beckurts and Otto [8] made a study of the thermal decomposition of the silver salts of mono-, di-, and trichloroacetic acids. They noted that the monochloroacetate yielded silver chloride and glycolide, which then turned into glycolic acid. As for the trichloroacetate, the authors give the following equations for its decomposition:



$$CCl_3\text{-}COOAg + H_2O \rightarrow C(Cl_2)\text{=}C(OH)\text{-}COOH + AgCl; \quad C(Cl_2)\text{=}C(OH)\text{-}COOH \rightarrow 2HCl + CO_2 + CO.$$

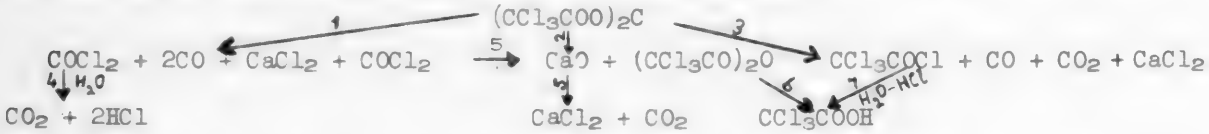
The thermal decomposition of sodium trichloroacetate has been studied in greater detail [9], phosgene, carbon dioxide, carbon monoxide, hexachloroethane, tetrachloroethane, trichloroacetic acid, and the latter's anhydride being recovered. After this paper, whose author, it should be said, uses formulas that are rather doubtful, such as no one else has, so



far as we know, done any comprehensive research on the thermal decomposition of chloro substitution derivatives of acetic acid.

In our experiments using calcium trichloroacetate, we secured: 1) the following gaseous products: carbon monoxide, carbon dioxide, hydrogen chloride, and phosgene; 2) the following liquid products: trichloroacetyl chloride and trichloroacetic anhydride; and 3) the following solid products: trichloroacetic acid, hexachloroethane, calcium chloride, and carbon.

The presence of trichloroacetic anhydride and trichloroacetic acid among the reaction products thus agrees with the general outline suggested by Bamdas and Shemyakin [4] for the thermal decomposition of salts. The latter of the two substances mentioned above was formed by the hydration of both trichloroacetic anhydride and trichloroacetyl chloride with water. But where did the water come from? An investigation of the calcium salt of trichloroacetic acid indicated that it was practically impossible to secure it in an absolutely anhydrous state. The salt is hygroscopic, retaining water tenaciously, even when dried for hours in a tube through which hot air was passed. As for the phosgene, it might be produced in the primary or secondary decomposition reactions of the substances already produced, as in the partial decomposition of trichloroacetic anhydride, which breaks down when heated to 215°, yielding phosgene [10]. The most interesting of the other end product is trichloroacetyl chloride. It is most expedient to assume that it was formed during the initial processes outside of the decomposition of the calcium trichloroacetate as specified by Bamdas and Shemyakin, as is indicated by the Engler and Stende experiments referred to above [7]. The end products thus give us the following outline of the decomposition of calcium trichloroacetate:



Of all these processes, 1 predominates, with 2 and 3 being of equal importance, as is evidenced by the following:

a) Phosgene and carbon monoxide are evolved energetically when calcium trichloroacetate is heated to as little as 150°, when no liquid products are as yet detectable; b) Equation 2 calls for the formation of calcium oxide, but its absence in the salt's calcination residue is explainable only if enough phosgene has been formed; and c) notwithstanding the large consumption of phosgene in Reactions 4 and 5, the gaseous products still contain some 10% of it.

The thermal decomposition of calcium monochloroacetate presents a much more highly complicated picture. In this reaction we secured the following

substances: 1) the following gaseous products: carbon monoxide, carbon dioxide, hydrogen chloride, methyl chloride, and ethylene; 2) the following liquid products: tar, phenol, and water; and 3) the following solids: glycolic acid, calcium chloride, calcium carbonate, and carbon.

The presence of tar, amounting to 8% of the salt used, and the presence of phenol are evidence of the extremely complex processes that take place during the thermal decomposition of calcium monochloroacetate, which we have not yet succeeded in deciphering. The finding of glycolic acid in the decomposition products is some evidence that the calcium chloroacetate decomposed as specified by Bamdas and Shemyakin, i.e., the initial anhydride turned into diglycolide, the latter ending up as glycolic acid:

$$(ClCH_2COO)_2Ca \rightarrow CaO + (ClCH_2CO)_2O \rightarrow \begin{matrix} H_2C-O-CO \\ | \quad\quad | \\ OC-O-CH_2 \end{matrix} \xrightarrow{H_2O} HOCH_2COOH.$$

It is not impossible, however, that the glycolic acid is formed otherwise: the calcium monochloroacetate decomposing like silver chloroacetate [4] into calcium chloride and glycolide, which is then hydrated to glycolic acid:

$$1)\ (ClCH_2COO)_2Ca \rightarrow CaCl_2 + \begin{matrix} H_2C-O-CO \\ | \quad\quad | \\ OC-O-CH_2 \end{matrix}$$

$$2)\ \begin{matrix} H_2C-O-CO \\ | \quad\quad | \\ OC-O-CH_2 \end{matrix} + 2H_2O \rightarrow 2HOCH_2COOH,$$

The only other product of the reaction we shall dwell upon is the ethylene. The presence of appreciable quantities of the latter (up to 24% by volume) in the gaseous products is evidence that it may be formed during the initial processes involved in the decomposition of the salt, i.e., the salt may be cleaved into ethylene, carbon dioxide, and calcium chloride, as follows:

$$\begin{matrix} ClCH_2COO \\ ClCH_2COO \end{matrix}\!\!>Ca \rightarrow \begin{matrix} CH_2 \\ \| \\ CH_2 \end{matrix} + 2CO_2 + CaCl_2$$

EXPERIMENTAL

The Thermal Decomposition of Calcium Trichloroacetate

28 g of calcium trichloroacetate, dried to constant weight at 85-90°, was placed in a 300-ml refractory retort fitted with a high-temperature thermometer. The retort was connected to five Drexel bottles, the last bottle being connected to a gasometer. The first Drexel bottle was empty, being intended to collect the liquid products coming from the retort. This bottle was chilled with cold water. The second and third Drexel bottles contained a saturated aqueous solution of aniline to trap the phosgene; the fourth bottle contained a 40% solution of sodium hydroxide; and the fifth contained baryta water. The gasometer contained a saturated solution of sodium chloride. The retort was gradually heated in an air bath; the salt fused at 125-130°, gas being evolved and the retort being filled with white fumes. The salt turned yellow at 150-155° and swelled up, large quantities of gas being evolved. At 170°, drops of a heavy oily liquid appeared in the first receiver, its quantity increasing sharply

at 200°, two layers of liquid beginning to collect in the receiver: the lower layer being a heavy oil, and the upper one aqueous. At 250°, only the lower layer of liquid and gases were evolved. At 300°, the formation of liquid and gaseous products dropped off sharply, the evolution of gases and liquid products usually coming to a stop at 400-420°. The run usually lasted 1 hour 40 minutes to 2 hours.

a) Analysis of the residue in the retort. The solid residue in the retort was a light porous mass weighing 7.03 g. The mass was treated with water and the solution filtered, 0 102 g of carbon (after drying) being left upon the filter. The soluble part totaled 6.93 g, consisting of calcium chloride, which was proved by determining the calcium and chlorine in the solution.

b) Analysis of the liquid in the first Drexel bottle. It weighed 9.66 g and consisted of two layers: the upper one being tansparent and aqueous and the lower one being dark, heavy, and oily. The layers separated slowly after the salt had decomposed the upper layer weighing 1.86 g and the lower 7.80 g. The upper layer, which displayed a strongly acidic reaction, was an aqueous solution of hydrogen chloride and trichloroacetic acid; 0.345 g of the latter was precipitated when the aqueous solution was boiled, it being identified by its characteristic properties [11]. The lower layer, which exhibited a strongly acidic reaction, was chilled with snow. The 1.334 g of resultant crystals were desiccated above sulfuric acid. The liquid residue left after this chilling was distilled in a Würtz flask, 2.4 g of a fraction with a b.p. of 114-121° being collected. This fraction had a pungent odor, fumed strongly in the air, and decomposed quantitatively into trichloroacetic and hydrochloric acids when allowed to stand with water, indicating the presence of trichloroacetyl chloride, the b.p. of which is given in the literature as 118° [12]. During distillation 1 7 g of crystals of trichloroacetic acid accumulated in the condenser tube. After the trichloroacetyl chloride had been driven off, the temperature in the flask was rapidly raised to 220° the liquid residue in the flask (totaling 0.6 g) boiling at 220-225° with decomposition and with the evolution of gases smelling of phosgene. This behavior of the residue indicated that it was trichloroacetic anhydride, which boils with decomposition at 222-224° according to the literature [13]. When these tests were repeated, the flask residue was not distilled, but reacted with a few drops of water, converting it wholly into trichloroacetic acid, which confirmed the foregoing hypothesis.

c) Analysis of the gases. Flocs of diphenylurea were formed in the Drexel bottle containing aniline water; they were filtered out, washed a few times on the filter with hot water, and dried to constant weight at 70-80°. The diphenylurea recovered totaled 2.05 g, equivalent to 0.955 g of phosgene absorbed. The diphenylurea fused at 235° and exhibited no depression when fused together with a known sample of this substance. Hydrogen chloride was found in all the Drexel bottles. Carbon dioxide was determined as sodium carbonate in the usual manner [14] in the fourth bottle, containing the 40% solution of sodium hydroxide. The gases collected in the gasometer had a volume of 2.55 liters at 15° and 752 mm pressure. Determinations were made of carbon monoxide and carbon dioxide, though none of the latter was found. The carbon monoxide was determined by absorbing the gas in an ammoniacal solution of cuprous chloride in an Orsat apparatus. Of 100 ml of the gas, 84.03 ml was absorbed, so that the gasometer contained 2.143 liters of carbor monoxide, or 2.008 liters under standard conditions, or 2.5 g. The rest of the gas in the gasometer was air, displaced from the retort and the wash bottles. As for the hexachloroethane, it was always found as a minute quantity of elongated crystals on the neck of the retort when the salt was decomposed. It was identified by its characteristic

properties [11].

The Thermal Decomposition of Calcium Monochloroacetate

32 g of calcium monochloroacetate, dried to constant weight at 85-90°, was decomposed as indicated in the previous instance. The liquid products of decomposition were collected in a water-chilled Drexel bottle, the gaseous products passing through two bottles containing a 40% sodium hydroxide solution, one bottle containing a solution of baryta water, one bottle containing benzene to absorb any fumes and tar that passed over at times, and finally entering a gasometer containing a saturated solution of sodium chloride. When the salt was heated to 105°, a slight quantity of water was driven off, while at 145° drops of a dark liquid appeared on the walls of the retort, which turned dark-purple at 175°. At the same time the salt swelled up considerably, beginning to give off yellow fumes. One hour after heating had begun, when the temperature had been raised to 190° a cloudy, tarry liquid began to collect in the receiver while the evolution of gas increased. The swelling up of the salt ceased at 250° and the evolution of gas diminished. Two hours and 40 minutes after heating had begun, the heating was stopped, at a temperature of 375°, inasmuch as no more gas or liquid products were being evolved.

a) Analysis of the flask residue. The 13.68 g of solid residue in the flask was treated with water, most of it dissolving; nothing but calcium chloride was found in the solution. The portion that did not dissolve in the water was thoroughly washed with water until the wash waters exhibited a negative reaction for the chlorine ion, and then it was dried. The residue weighed 1.95 g; hence, the calcium chloride totaled 11.73 g. The residue was treated with a solution of hydrochloric acid, a gas which proved to be carbon dioxide, was evolved, indicating that the residue contained calcium carbonate. Some of the residue did not dissolve in this treatment, however; this portion of the residue proved to be carbon, which weighed 0.31 g after being filtered out and dried. Thus calcium carbonate accounted for 1.64 g.

b) Analysis of the liquid in the first Drexel bottle. The liquid products totaled 11.2 g; they separated after a short time into a greenish-brown tar and an aqueous liquid. They smelled like pitch and displayed an acid reaction with litmus paper. The tar was separated from the rest of the liquid by chloroform extraction; the latter was driven off, leaving a residue of 2.39 g, or 7.4% by weight of the salt decomposed. The tar was insoluble in water, though freely soluble in organic solvents; it darkened and grew thick when allowed to stand. It contained no chlorine, burned with a very smoky flame, and dissolved partially in alkalies (0.174 g, or 7.3% of the tar by weight). The watery liquid separated from the tar was strongly acidic and contained hydrochloric acid, phenol, and glycolic acid. The presence of the glycolic acid was demonstrated, first, by the formation of formaldehyde when part of the evaporated watery liquid was heated with sulfuric acid, and second, by the melting point of the precipitated crystals (76-77°, the figure given in the literature being 79-80°) and microchemically as the calcium salt [15]. The phenol was determined in the watery layer by adding a concentrated solution of potassium hydroxide to part of the latter until its reaction was slightly alkaline, after which carbon dioxide was passed through the resultant solution, and the liquid was extracted with ether. After the ether had been evaporated, bromine water was added to the residue. This threw down tribromophenol, with its typical odor, and a m.p. of 94-95° (the literature gives the m.p. as 95°).

Analysis of the gases. The second and third Drexel flasks absorbed the hydrogen chloride and the carbon dioxide, which were determined in the usual

manner [14]. The carbon dioxide totaled 2.22 g. The gases collected in the gasometer occupied a volume of 2.45 liters at 15° and 752 mm. The presence of ethylene in these gases was established by absorption in bromine water, that of carbon monoxide by absorption in an ammoniacal solution of cuprous chloride, and that of methyl chloride by absorption in glacial acetic acid. Of 100 ml of gas, the bromine water absorbed 47.55 ml, the ammoniacal solution of cuprous chloride absorbed 29.40 ml, and the glacial acetic acid absorbed 8.90 ml, or a total of 85.85 ml. Hence, the total volume of gases contained: 1.16 liters of ethylene, or 1.36 g; 0.72 liter of carbon monoxide, or 0.84 g; and 0.22 liter of methyl chloride, or 0.47 g; or a total of 2.67 g. Hence, the decomposition products may be summarized as follows (without the free hydrogen chloride): 32 g of the original salt (or 100%); 13.68 g of solid residue (42.31%); 9.79 g of liquid (30.28%); 4.89 g (total) of gases (15.12%), aggregating 87.71%. Hence, the free hydrogen chloride in the aqueous solution in the first four Drexel bottles accounted for 12.29%, or 3.97 g.

SUMMARY

1) The calcium salts of halogenated acids decompose in a much more complicated fashion than a salt of the coresponding unsubstituted acid.

2) The decomposition temperature of halogenated acids is much lower than the decomposition temperature of the corresponding unsubstituted acid.

3) No ketones are formed when calcium salts of halogenated acids were decomposed.

4) The calcium salts of halogenated acids are partially decomposed in accordance with the outline suggested by Bamdas and Shemyakin, a metallic oxide and an acid anhydride being formed.

5) The formation of phenol from derivatives of acetic acid has been observed for the first time.

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Received December 12, 1949.

1974

THE MECHANISM OF THE CATALYTIC ACTION OF ALUMINUM CHLORIDE

II. THE STRUCTURE OF COORDINATION COMPOUNDS WITH ACID HALIDES, KETONES, AND OTHER OXYGEN COMPOUNDS

N. N. Lebedev

Aluminum chloride forms stable coordination compounds with acid chlorides and ketones many of them being crystalline substances. The thermal analysis of these systems performed by Menshutkin [1] established the following formulas for these compounds:

$$RCOCl \cdot AlCl_3 \text{ and } ArCOR \cdot AlCl_3.$$

Meerwein [2] has proposed the following structural formulas for acid chloride coordination compounds:

$$R-\underset{\underset{O}{\|}}{C}-\ddot{\underset{\cdot\cdot}{Cl}}:AlCl_3 \quad \text{or} \quad [RCO] + [AlCl_4]^-,$$

which have been universally adopted.

Fairbrother [3] tested the exchange of halogen atoms to corroborate this formula, but his results seem to us to be not very convincing, being explainable rather by thermodynamic factors.

We have made a spectroscopic and thermochemical study of compounds of aluminum bromide with acid bromides and ketones in order to ascertain the structure of these coordination compounds.

Absorption spectra of coordination compounds. The absorption of light by aluminum chloride in the ultraviolet region has been investigated only in aqueous solutions [4]. It was found that the absorption of aluminum chloride is very weak, its boundary being located at 2800 A. This makes it possible to neglect the absorption of the aluminum halides themselves henceforth; confirmation of this is likewise found in the results of our research on the ultraviolet spectra of solutions of aluminum bromide in ethyl bromide [5].

Aluminum bromide was employed instead of the insoluble chloride, ethyl bromide being used as the solvent. The ethyl bromide was thoroughly purified by sulfuric acid and repeated distillation, only the middle fractions being taken. The aluminum bromide was prepared from aluminum chips and bromine; it was distilled until a colorless product was obtained, which was stored in sealed ampoules. The organic compounds used in our tests were: n-butyryl bromide, acetophenone, and benzophenone, the first being refined by means of repeated distillation, the second being refined by freezing, and the third by recrystallization.

The spectra of an organic compound and of its coordination compound with aluminum bromide were recorded on the same plate at various concentrations, but with the cell thickness kept constant at 1 mm. Then the photos were compared microphotometrically with black marks that had been photographed with a Scheibe rotating sector for the pure solvent.

The absorption curves of n-butyryl bromide and of its coordination compound with aluminum bromide, at equimolecular proportions and with a 100% excess of the latter, are shown in Figure 1. Formation of the coordination compound results in

a shift of the absorption region by about 200 A toward the longer wavelengths of the spectrum, an excess of aluminum bromide having the same effect.

A similar state of affairs, though even more pronounced, was observed with the ketones. The absorption curves of acetophenone and of its coordination compound with aluminum bromide are reproduced in Figure 2. Here the absorption region is shifted by 700 A though in this case we employed a large excess of the bromide, since we feared the latter would be hydrolyzed if its concentration were low.

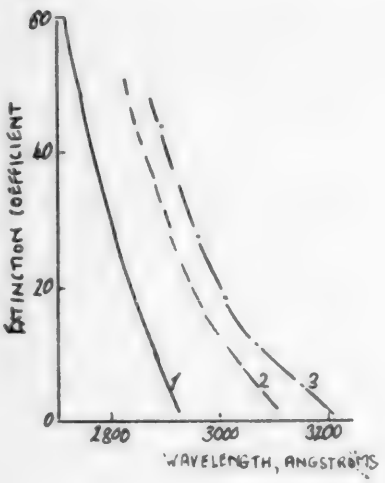


Fig.1.

We managed to secure a curve for the pure coordination compound for benzophenone (Figure 3), even if only for a small portion of the spectrum. It exhibited a

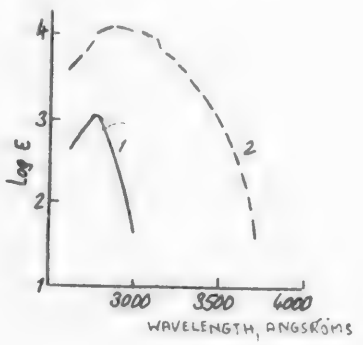


Fig.2.

shift of the beginning of absorption by 400 A as against that for benzophenone. An excess of aluminum bromide increases this displacement even more than in the case of acetophenone, namely, by 1000 A Under these conditions, the benzophenone coordination compound begins to absorb light even in the visible portion of the spectrum.

It is worthy of note that the absorption curve of the coordination compound of aluminum bromide and benzophenone secured by us is nearly identical with the absorption curve of benzophenone in sulfuric acid solutions [6]. This is evidence of the great similarity between the structure of the addition products of ketones and aluminum chloride and that of ketones and acids.

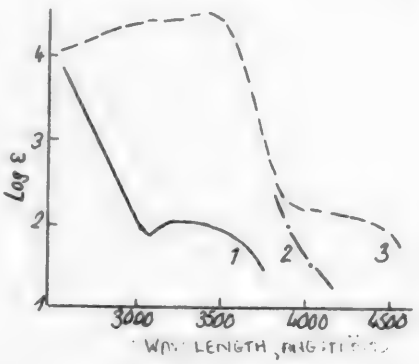


Fig.3.

Heat of formation of coordination compounds. The calorimeter used was a 250-ml Dewar flask, placed in a thermostat. The entrace of moisture was prevented by sealing the flask with a rubber stopper, fitted with a Beckmann thermometer a charging device, and a stirrer equipped with a mercury seal 1,2-Dibromoethane was used as the calorimetric liquid, the dibromoethane being charged into the calorimetric vessel, and the aluminum bromide being dissolved in it. A weighed batch of the acid bromide or ketone was added to the resulting

solution, the heat evolved in the formation of the coordination compound being measured in the usual manner.

This procedure was used to measure Q, the heat of the reactions of n-butyryl bromide, benzoyl bromide, acetophenone, and benzophenone with the aluminum bromide dissolved in the dibromoethane (Table 1). We made parallel determinations of the heat of solution of the coordination compounds in dibromoethane (q_k) in order to compute the heat of formation of the coordination compounds in the standard state. They were prepared by mixing together equimolecular quantities of the components dissolved in carbon disulfide, and then blowing a current of anhydrous air through the solution. Only the coordination compounds of benzoyl bromide and benzophenone were secured as solids, the coordination compounds of butyryl bromide and acetophenone being viscous liquids. Their heats of solution in dibromoethane are listed in Table 2.

TABLE 1

Test temperature	Grams of organic compound	Δt°	Heat evolved, calories	Q, Cal/mol
		n-Butyryl bromide		
21.9°	2.04	+2.727	148.1	10.96
22.3	2.28	+2.955	167.03	11.05
23.3	1.84	+2.304	135.9	11.15
		Benzoyl bromide		
20.05	2.00	+2.258	148.7	13.75
21.1	3.25	+3.485	238.6	13.58
		Acetophenone		
22.2	1.53	+4.146	286.1	22.50
21.75	1.25	+3.387	232.46	22.30
		Benzophenone		
22.07	1.05	+1.865	111.2	19.28
22.08	0.74	+1 312	81.34	20.04
22.56	1.47	+2.398	154.87	19.20

TABLE 2

Test temperature	Grams of coordination compound	Δt°	Heat evolved or absorbed, cal	q_k Cal/mol
		$n\text{-}C_3H_7COBr \cdot AlBr_3$ (liq.)		
22.4°	8.72	-0.037	1.44	+0.07
21.0	9.75	-0.027	1.83	+0.08
		$C_6H_5COBr \cdot AlBr_3$ (solid)		
19.55	11.80	-1.299	-70.18	-2.67
20.25	7.65	-0.827	-46.4	-2.74
		$C_6H_5COCH_3 \cdot AlBr$ (liq.)		
22.6	17.64	-0.12	-0.68	+0.02
21.4	13.45	+0.03	-0.35	-0.10
		$C_6H_5COC_6H_5 \cdot AlBr_3$ (solid)		
22.1	8.97	-0.807	-45.56	-2.28
21.9	8.44	-0.816	-48.1	-2.55
22.4	7.62	-0.783	-40.42	-2.38

These results enabled us to calculate the heat of reaction in the formation of the coordination compounds for the standard state of the intial and end products by means of the following equations:

$$AlBr_3 \text{ (solid)} \longrightarrow AlBr_3 \text{ (diss.)}; \qquad -\Delta H_1 = +q_p;$$
$$AlBr_3 \text{ (diss.)} + RCOX \longrightarrow RCOX \cdot AlBr_3 \text{ (diss.)}; \quad -\Delta H_2 = Q;$$
$$RCOX \cdot AlBr_3 \text{ (diss.)} \longrightarrow RCOX \cdot AlBr_3; \qquad -\Delta H_3 = -q_k.$$
$$AlBr_3 \text{ (solid)} + RCOX \longrightarrow RCOX \cdot AlBr_3; \qquad -\Delta H^\circ = q_p + Q - q_k.$$

the last equation representing the crystalline state of the benzoyl bromide and benzophenone coordination compounds and the liquid state of the butyryl bromide and acetophenone coordination compounds. The original organic compounds were also liquids, with the exception of the benzophenone.

The final mean results of our measurements are given in Table 3, which also lists the heat of solution of aluminum bromide in dibromoethane q_p [7] at the concentrations employed in determining the heats of reaction.

TABLE 3

Organic compounds	Σ Cal/mol	q_k Cal/mol	q_p Cal/mol	ΔH° Cal/mol
n-Butyryl bromide	11.05	+0.07	-1.9	9.1
Benzoyl bromide	13.7	-2.7	-2.1	14.3
Acetophenone	22.4	0	-2.0	20.4
Benzophenone	19.5	-2.4	-2.0	19.9

Evaluation of Results. A study of the absorption spectra has shown that the same phenomenon, consisting in a shift of the absorption region toward the longer wavelengths of the spectrum, is observed when aluminum bromide enters into coordination compounds with ketones or acid bromides, the differences in their spectroscopic behavior being solely quantitative. This becomes particularly clear when we bear in mind that the dissolution of aluminum bromide in ethyl bromide produces only a minute displacement of the absorption region [5], which sharply distinguishes the halogen derivatives from the ketones and acid chlorides.

The results of our thermochemical investigations were similar. Comparison of our findings indicates that the heats of formation of the coordination compounds of aluminum bromide with acid bromides and ketones, though they are all different, are quantities of the same order of magnitude, the differences between them being due to secondary causes rather than to any fundamental difference in the type of bond The heats of solutions of the aluminum bromide in halogen derivatives – substances that contain only a halogen function, but no oxygen atom – are very less than these values, sometimes even being negative [7]. All this indicates that in organic compounds an oxygen atom displayes a much greater tendency to attach itself to aluminum chloride than a halogen atom does, and that there is no reason to suppose that this rule may be violated in mixed compounds, no matter what the acid chloride may be. This inference is corroborated by the high stability of coordination compounds of aluminum chloride with acid halides, which is typical of oxygen compounds (ketones, sulfones, nitro compounds, ethers, and the like) in contrast to the instability of its coordination compounds with halogen derivatives.

Measurements of the dipole moments of coordination compounds of aluminum halides with ketones ethers, acid halides, and nitrobenzene [8] likewise bear out this viewpoint of ours. We found that the dipole moments of the coordination compounds are larger than those of the original substances, the difference between the two being the same for all the compounds specified above. This is evidence that the type of bond linking the aluminum chloride in these coordination compounds is always the same.

Our findings thus afford sufficient proof that aluminum chloride is added to the oxygen atom in the formation of coordination compounds with acid halides as well as with ketones. Hence the widely accepted Meerwein formula must be regarded as false.

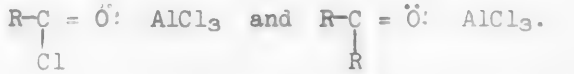
What is more, our spectroscopic data furnish a decisive argument against the formulas for these coordination compounds proposed in their time by Gustavson [9] and Kronberg [10], who believed that the aluminum chloride was added at the double bond of the carbonyl group:

$$R_2CCl{-}OAlCl_2 \quad \text{and} \quad RCCl_2{-}OAlCl_2$$

It is obvious that this would cause the basic chromophore, on which the light absorption of carbonyl compounds depends to disappear, so that coordination compounds would absorb light in a shorter-wavelength region of the spec-

trum than was the case in the original substances. As a matter of fact, exactly the contrary phenomenon is observed, testifying to the erroneousness of these formulas.

The coordination compounds we are concerned with are actually formed at the expense of the unshared electron pair of the oxygen atom in ketones or acid halides, the aluminum atom being required to complete the electron shell of the oxygen atom:

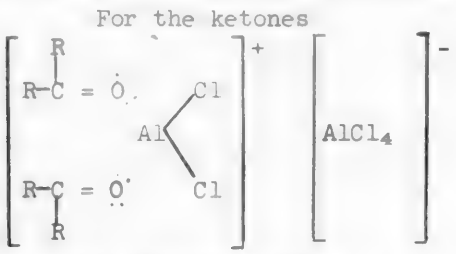


These formulas are still at variance, however, with two well-known experimental facts, Wertyporoch and Firla [11] have found that the coordination compounds of aluminum chloride with ketones and acid halides are ionic compounds, the conductance of which approaches that of true salts. Moreover, Kohler and Ulich made ebullioscopic measurements in carbon disulfide and cryoscopic measurements in benzene, finding that these coordination compounds, like the aluminum halides, possess double molecular weight, being converted into monomers only when the dilution is high enough.

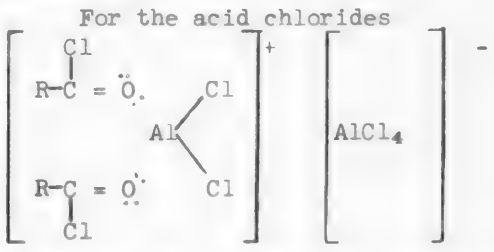
We therefore believe that aluminum chloride reacts in its dimer form when entering into coordination compounds, dissociating as follows when acted upon by ionizing substances (in contrast to thermal dissociation):

The first of the aluminum atoms then completes its electron shell, linking itself to the oxygen atom in the ketones or acid halides. This results in the following formulas for the coordination compounds:

For the ketones



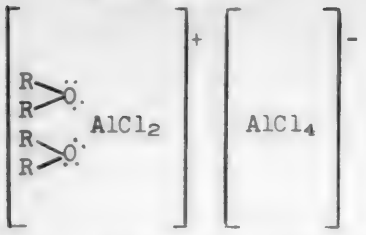
For the acid chlorides



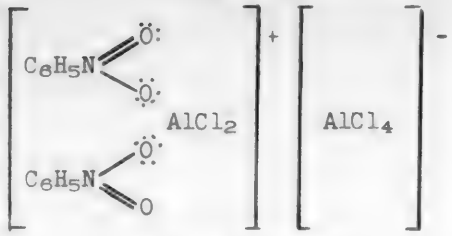
which agree perfectly with all the experimental data. They explain the high dipole moments of these compounds, as well as their excellent conductance. The coordination compounds exist as ionic pairs in concentrated solutions, exhibiting double molecular weight, while they dissociate into ions in dilute solutions. Looked at in this manner, the monomeric forms of these coordination compounds do not exist at all.

The coordination compounds of aluminum halides with ethers, nitrobenzene, sulfones, and sulfochlorides also have a double molecular weight [12, 13], so that we assign them the following formulas, by analogy with the foregoing:

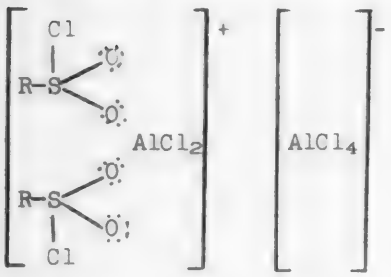
With ethers:



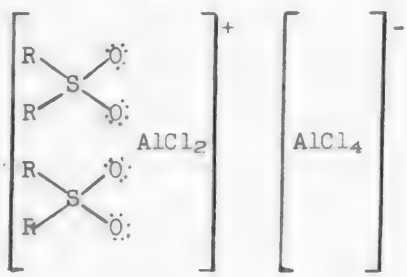
With nitrobenzene:



With sulfochlorides:



With sulfones:



It is likely that the other coordination compounds of the aluminum halides are constructed in the same way.

In conclusion, the author wishes to express his profound thanks to Ast. Prof. Yu. Ya. Mikhailenko for his valuable assistance in the spectroscopic investigations and to Prof. V. V. Korshak for his interest in this research project, which greatly aided in carrying it out.

SUMMARY

1. The ultraviolet absorption spectra of the coordination compounds of aluminum bromide with n-butyryl bromide, acetophenone, and benzophenone have been recorded. It has been found that the formation of these coordination compounds involves an appreciable shift of the absorption region to the longer wavelengths of the spectrum.

2. The heats of formation of the coordination compounds of aluminum bromide with n-butyryl bromide, benzoyl bromide, acetophenone, and benzophenone have been determined.

3. It has been shown that aluminum chloride is attached to the oxygen atom in coordination compounds with acid chlorides. Hence, the Meerwein formula is to be regarded as erroneous.

4. New formulas are put forward for the coordination compounds of aluminum chloride with acid halides, ketones, and other organic substances, in the light of the ionic nature of these compounds, their conductance, and their being dimers.

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Received August 9, 1948.

THE INFLUENCE OF BORON FLUORIDE UPON THE CRACKING OF HYDROCARBONS

Ya. M. Paushkin and Yu. S. Lipatov

The action of boron fluoride as a catalyst has been investigation in detail in polymerization, alkylation, condensation, sulfonation, and nitration reactions [1, 2, 3]. Almost no work at all has been done on the effect of boron fluoride upon cracking, though we know that several halides, such as aluminum chloride and bromide, ferrous chloride, and (in part) zinc chloride, are cracking catalysts [4].

The literature contains two very brief references to the part played by boron fluoride in cracking. A German patent [5] states that boron fluoride may be employed as a catalyst in the cracking of crude petroleum at 380° and a pressure of 150 atm. A paper by Fridman [6] asserts that no changes were observed in the fractional constitution or specific gravity of the original kerosene when it was cracked in the presence of BF_3.

The present paper reports on the cracking of Diesel fuel in the presence of boron fluoride with activated charcoal and an aluminosilicate catalyst.

EXPERIMENTAL

The research on the cracking process was carried out in the apparatus depicted in Fig. 1. (For Fig. see Plate, page. 2137.)

The reactor – the principal part of the apparatus – consisted of a glass tube 30 mm in diameter, through which there passed a thin glass tube (the jacket for the thermocouple). The reactor was heated by an electric heating coil, insulated on the outside with asbestos. The temperature was controlled by means of a rheostat, being held to within $\pm 2°$ of the desired temperature during the run. The upper part of the tower was filled with small glass rods and served as a heat exchanger, the lower part being filled with charcoal or an aluminosilicate catalyst, which occupied a volume of 225 ml. The liquid raw material was fed in at the uniform rate of 60 ml per hour, or 0.24 volume per volume of the catalyst, directly from a graduated buret or from a buret connected to a constant-level device. The boron fluoride, totaling 10% of the raw material, was uniformly fed into the reactor from a special device, in which it was produced by decomposing the etherate of boron fluoride and anisole at 180-190°. The supply of boron fluoride was regulated by controlling the amount of the etherate of boron fluoride released from the gradulated buret for decomposition.

The liquid cracking products were collected in a receiver connected to a reflux condenser, while the boron fluoride was collected in wash bottles filled with anisole. The cracking gas was collected in a gasometer The whole system operated under a vacuum of a few millimeters of water column, which was regulated by the quantity of water flowing out of the gasometer overflow valve. The raw material used for cracking was a Diesel fuel that had a sp. gr. d_4^{20} of 0.8448 and the following fractional composition:

Boiling begins..... 140°
10% distillate..... up to 176 40% distillate..... up to 250°
15% distillate..... 200 50% distillate..... 265
20% distillate..... 220 85% distillate..... 324

After cracking was complete, we determined the distillate yield (this usually totaled 85-95% by volume, depending upon the cracking temperature), the specific gravity, the bromine number, the gas yield, the fractional composition of the distillate and its percentage of unsaturated compounds.

The experimental data listed in Table 1 show that when boron fluoride is used for cracking with activated charcoal, it cuts the gasoline yield obtained with charcoal alone nearly in half, lowers the bromine numbers of the cracking gasoline appreciably, and diminishes the yield of cracking gas and its percentage of unsaturated compounds. When "cracking" is done with activated charcoal and boron fluoride at 350-450°, the distillate is heavier than the original raw material.

TABLE 1

Results of Experiments on Cracking with Activated Charcoal

Test No.	Catalyst	Distillate yield, (%)	Test temperature	Sp. gr. of cracking product	Br. No. of gasoline	Cracking gas		Temperature at which 50% of the distillate is obtained	Per cent yield of gasoline, up to 20°
						Yield in liters per 100 g raw material	Unsaturated compounds, %		
1	Charcoal + BF_3	97	350	0.8516	4	1.2	None	270	13
2	Charcoal + BF_3	94	400	0.8440	3.5	0.8	4	278	30
3	Charcoal.....	–	460	0.8247	20	5.6	8	258	39
4	Charcoal + BF_3	96	460	0.8449	10	2.2	5	276	11
5	Charcoal.....	89	500	0.8335	44	14	–	220	41
6	Charcoal + BF_3	89	500	0.8493	9	–	–	258	22
7	Charcoal.....	80	560	0.8445	60	17.6	29	228	31
8	Charcoal + BF_3	85	560	0.8440	40	9.7	19	260	17

This is attributable to the condensing, polymerizing, and alkylating properties of boron fluoride, which result in condensation of the original raw material (Tests 1, 2, and 4) or in diminishing the extent of its decomposition above 450°, as may be seen in the fractionation curves (Figs. 2 and 3).

An altogether different state of affairs prevailed when cracking was done with an aluminosilicate catalyst in the presence of 10% boron fluoride. In this case the reactor column was filled with the aluminosilicate cracking catalyst (210 ml), the raw material being put through at the rate of 0 285 volume of raw material per volume of catalyst per hour. The test lasted 80 minutes, after which the catalyst was regenerated for 8-10 hours by passing air through it at 500-540° to burn away the carbon from the surface of the catalyst.

The test Results are listed in Table 2.

The figures in Table 2 indicate that boron fluoride greatly activates the aluminosilicate catalyst, increasing the gasoline yield some 15-45%, depending on the cracking temperature, the gasoline produced being lighter. The

TABLE 2

Results of Experiments on Cracking with an Aluminosilicate Catalyst and Boron Fluoride

Test No.	Catalyst	Distillate yield, %	Test temperature	Specific gravity of cracking product	Bromine No. of gasoline (up to 200°.	% Unsaturated compounds in cracking gas	Temp. at which 50% of distillate is secured	% Yield of gasoline, up to 200°.
1	Aluminosilicate.....	55	310	0.8102	2.5	-	245	25
2	Aluminosilicate + BF_3	54	310	0.8206	3	-	-	25
3	Aluminosilicate.....	77	350	0.8008	2.5	None	240	33
4	Aluminosilicate + BF_3	78	350	0.7877	5.5	None	-	48
5	Aluminosilicate.....	79	400	0.8060	10	18	210	48
6	Aluminosilicate + BF_3	77	408	0.7867	6	5	179	60
7	Aluminosilicate.....	73	440	0.8091	18	12	202	48
8	Aluminosilicate + BF_3	63	440	0.7938	11	9	174	60
9	Aluminosilicate.....	47	510	0.8388	18	7	195	54
10	Aluminosilicate + BF_3	47	510	0.8196	8	4	170	61

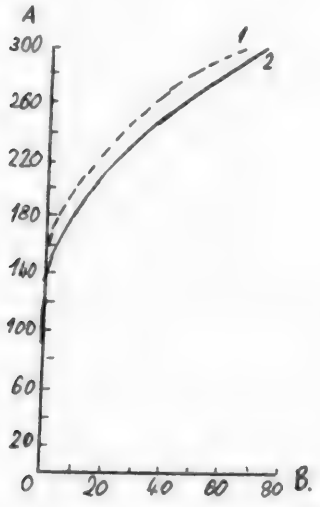


Fig. 2. Fractional composition of Diesel fuel before and after cracking with activated charcoal and BF_3 at 395°.

A - Temperature, (° C); B - fractional composition, per cent by volume. 1 - charcoal + BF_3; 2 - original raw material.

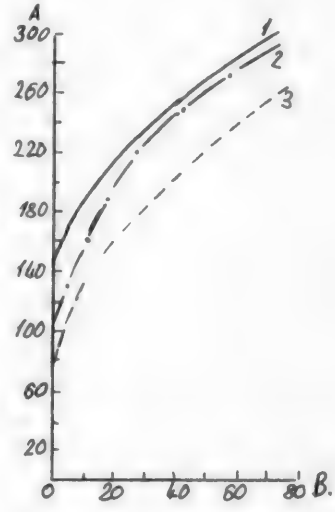


Fig. 3. Fractional composition of Diesel fuel before and after cracking with activated charcoal and BF_3 at 500°.

A - Temperature, (° C); B - fractional composition, per cent by volume. 1 - original raw material; 2 - charcoal + BF_3; 3 - charcoal.

specific gravity of the distillate secured by cracking with boron fluoride is lower than that secured with the aluminosilicate catalyst alone. The fractional composition of the distillates and the specific gravity of the gasoline are shown in Figs. 4 and 5.

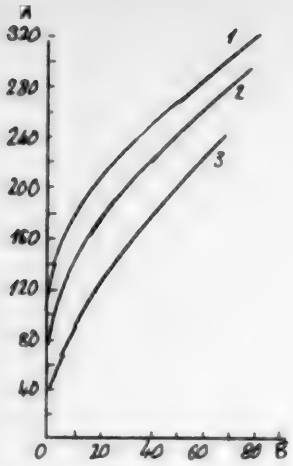


Fig. 4. Fractional composition of Diesel fuel before and after cracking with various catalysts at 350°.

A - Temperature, (° C); B - fractional composition, % by volume. 1 - original raw material; 2 - aluminosilicate; 3 - aluminosilicate + BF_3.

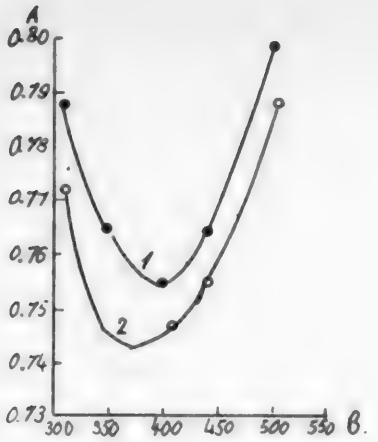


Fig. 5. Specific gravity of gasoline as a function of temperature.

A - Specific gravity; B - temperature, (° C): 1 - aluminosilicate; 2 - aluminosilicate + BF_3.

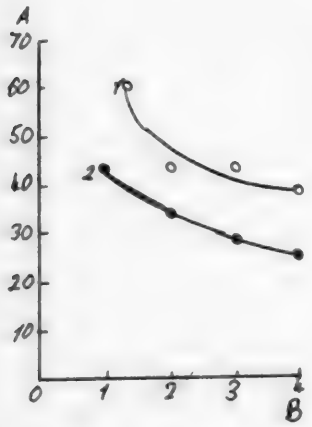


Fig. 6. Change in catalyst activity with time.

A - Gasoline yield, per cent; B - time, hours. 1 - Aluminosilicate + BF_3; 2 - aluminosilicate.

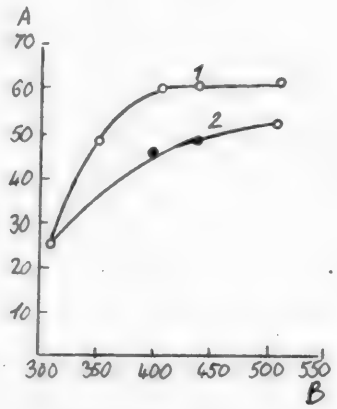


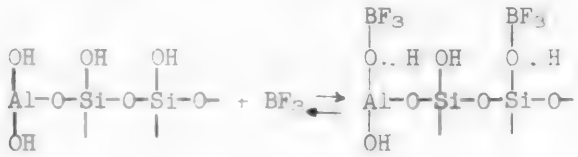
Fig. 7. Gasoline yield with various catalysts as a function of temperature.

A - Gasoline yield, per cent; B - temperature, (° C). 1 - Aluminosilicate + BF_3; 2 - aluminosilicate.

It is worthy of note that, beginning at 400°, the percentage of unsaturated compounds in the cracking gasoline and cracking gas produced with aluminosilicate plus boron fluoride is half that produced with the aluminosilicate alone. The octane number (by the Motor method) of cracking gasoline produced with the aluminosilicate catalyst was 65.1, while that produced with the aluminosilicate catalyst + BF_3 was 66.8, or somewhat higher.

We also made a study of the change in the activity of the aluminosilicate catalyst with time. This was done by determining the yield of gasoline with a boiling point up to 200° in the distillate every hour as cracking proceeded (Fig. 6). The gasoline yield is plotted as function of temperature in Fig. 7.

Our experimental findings indicate that the change in catalyst activity with cracking time is the same for the aluminosilicate catalyst alone as for the aluminosilicate plus boron fluoride, though the activity of the aluminosilicate catalyst remains somewhat higher when boron fluoride is present. Several authors [7, 8] believe that the activity of silicate cracking catalysts is due to their acidic properties. As they see it, the activation of an aluminosilicate catalyst by boron fluoride would be due to the increase in the former's acidic properties as a result of the formation at the catalyst surface of coordination compounds of the BF_3 with the hydroxyl groups in the silicic acid and the aluminum hydroxide.



The coordinated compounds may be unstable, decomposing again. It is probable that a coordination compound of boron fluoride may also involve the catalyst's binding of water.

As has been shown by Topchiev and Paushkin [3], the formation of coordination compounds of boron fluoride and hydroxyl groups results in the appearance of or an increase in the compounds' catalytic activity. The oxygen atom in the coordination compound becomes trivalent, weakening its bond to the proton:

The compound becomes a strong acid, the appearance of the protons causing the catalysis.

The acidity of the catalyst cannot be increased when activated charcoal is employed for cracking, the polymerizing action of the boron fluoride making its appearance; this condenses the original raw material, thus retarding cracking.

SUMMARY

1. Cracking with activated charcoal is retarded at temperatures above 450° when boron fluoride is present, while at temperatures of 400-450° and below, the original raw material is condensed, the yield of lighter fractions being reduced below their percentage in the raw material, which is attributable to the polymerizing action of the boron fluoride.

2. The state of affairs is different when cracking is done with an aluminosilicate catalyst in the presence of boron fluoride.

3. Products containing a lower percentage of unsaturated compounds are secured when cracking is done with boron fluoride present, whether activated charcoal or aluminosilicate is used as the catalyst.

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Received January 10, 1951.

TRANSFORMATIONS OF HYDROCARBONS WITH OXIDE CATALYSTS

IV. DEHYDROGENATION OF THE BUTANES WITH A CHROME CATALYST

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The results of numerous researches on the contact dehydrogenation of n-butane and isobutane have been published during the past twenty years. Surveys of these researches may be found in the generally accessible books by Obryadchikov [1] and Kiselev [2], to which we refer those interested in the history of the problem.

To judge by the data in the literature, chromic oxide deposited on alumina by simultaneous precipitation is the best catalyst for dehydrogenating the butanes.

Ignoring the papers dealing with the dehydrogenation of the butanes with other catalysts, we shall discuss a few papers published in recent years and dealing with the dehydrogenation of the butanes by chromic oxide deposited on alumina, which have not been discussed in the surveys mentioned.

Riesz, Pelican, and Komarewsky [3] compared the dehydrogenation of n-butane and isobutane with catalysts prepared in various ways and concluded, in agreement with the earlier researchers, that the best catalysts are prepared by the simultaneous precipitation of chrome and aluminum hydroxides.

Bloch and Schaad [4] attempted to emply mechanical mixtures of catalysts – chromic oxide deposited on alumina, and aluminosilicate promoted with thorium oxide – for the transformation of n-butane into isobutylene, i.e., to effect the dehydrogenation of n-butane and the isomerization of n-butylene in the same reactor. The authors found that the isomerization varied from 1% to 26.6% at 500 and 550°, depending on the length of the run and the contact time; they arbitrarily attributed the formation of isobutylene to the isomerizing properties of the aluminosilicate. This explanation cannot be accepted because the chrome catalyst possesses considerable isomerizing ability, as will be reported on at length in the experimental section of the present paper.

EXPERIMENTAL

n-Butane. The methane-hydrogen, ethane-ethylene, and propane-propylene fractions were driven out of the commercial butane-butylene fraction by using a copper low-temperature rectifying column [5, 6]. The waste butane-butylene fraction was successively passed through a scrubber containing concentrated sulfuric acid, a Tishchenko bottle filled with bromine water, another filled with an alkali solution, and a third filled with granulated calcium chloride. As the result of several runs we accumulated 700 ml of the butanes (in the liquid state).

The butane was recovered from the butane mixture, containing about 7% of isobutane, by means of a column specially assembled for this purpose, 144 cm high, 2 cm in diameter, fitted with a vacuum jacket. The packing consisted of one-turn copper rings 5 mm in diameter, made of 0.5 mm wire. The top of the

column was chilled with liquid air. The gas was passed through at the rate of 4 liters per hour, the bottoms totaling 60 drops per minute. The isobutane distilled over at 12.2°, the n-butane distilling at -0.5° (recomputed for 760 mm). Several rectification runs yielded a total of 300 ml of n-butane (liquid), whose critical solution temperature in nitrobenzene was 38.2°, while a liter (of the gas) weighed 2.59 g.

Isobutane. The raw material used was a 98% isobutylene, recovered in an industrial installation from the butane-butylene cracking fraction via trimethylcarbinol and specially refined in a Podbielnyak column. The isobutylene was hydrogenated with a nickel catalyst on kieselguhr, which had first been reduced with hydrogen. The hydrogenation temperature was 180-200°, the rate of feed being 2.5 mols of isobutylene and 10 ml of hydrogen per liter of catalyst per hour. The resultant isobutane was freed of any traces of unreacted isobutylene by treatment with bromine water and alkali, after which it was desiccated with calcium chloride and rectified in the same column that was used for the n-butane. We secured 250 ml of isobutane (liquid), its critical solution temperature in nitrobenzene being 60.6° and a liter (of the gas) weighing 2.59 g.

In our tests of butane dehydrogenation we used a chrome catalyst prepared by simultaneously precipitating aluminum and chromium hydroxides from an alkaline solution. The catalyst was charged into the reactor as pieces 3-4 mm in size. The tests were run in a circulating apparatus, the main element of which was the reactor, a quartz tube with an I.D. of 15 mm. To maintain a zone with a constant heating temperature within the tube, it was placed in a duraluminum block 30 cm long, in which a hole the size of the tube's outer diameter had been drilled. The temperature was measured with a carefully calibrated nichrome-constantan thermocouple.

The top of the tube was filled with pieces of broken porcelain to ensure better preheating of the butanes. The catalyst, totalling 15 cu cm was placed at the tail end of the tube. The sealed end of the thermocouple pocket, made of a thin-walled porcelain tube 5 mm in diameter, was placed at the entrance to the reaction zone. The temperature was measured at various points within the reaction space by sliding the thermocouple inside the pocket.

The n-butane or isobutane was supplied from a gasometer via a Tishchenko bottle containing sulfuric acid and via calcium chloride tubes. The rate of feed of the butanes was measured by means of a flow meter. Gas was tapped off during the run as required, using gas pipets filled with mercury. The exhaust gas was collected in a graduated gasometer.

The effect of the packing was determined before the runs were started. We tested broken glass, duraluminum chips, and broken porcelain. The waste gas contained 3% of unsaturated hydrocarbons when the temperature was 500° and the rate of n-butane feed was 3 liters per hour, no matter what packing was used, the percentage falling to 2% at a feed rate of 7 liters. When the temperature was raised to 550° and the feed rate was 3 liters, the unsaturated hydrocarbons rose to 5-6%. The volume of the unsaturated hydrocarbons in the exhaust gas corresponded to the volume of the exhaust hydrogen, within the limits of experimental accuracy.

It was found in preliminary tests that when the temperature was 550° and the feed rate was 3 liters per hour, the operation of the catalyst became constant after half an hour had elapsed; we therefore evacuated the exhaust gas into the draft system for the first half-hour in our major runs.

After each run the catalyst was regenerated with air drawn through by a water-jet pump. Regeneration lasted two hours as a rule (some 100 liters of air

being drawn through), after which well-purified hydrogen was passed over the catalyst for a certain length of time. The gas produced in the experiment was subjected to low-temperature rectification, the fractions collected being analyzed by the absorption method and the per cent hydrogen being determined by combustion over cupric oxide [6]. In not a single instance was any of the "second" (ethane-ethylene) fraction collected during rectification. In some runs some 30 cu cm of gas was driven off in the -65 to -25° range; this was taken to be the propane-propylene fraction, though it might have been better to regard it as an "intermediate fraction" between hydrogen and butane-butylene. The bulk of this fraction consisted of butane and butylenes, judging by its weight per liter – 2.53 g. As a rule 4.5 liters of gas were rectified. No liquid residue was found in any of the gas samples rectified.

In two instances (Tests 9 and 13 in Table 2) the mixture of butanes left after the undetermined hydrocarbons had been absorbed in bromine water was desiccated with phosphoric anhydride, burned, and analyzed by determining its consolute temperature in nitrobenzene. The composition of the mixture was calculated by the additivity rule.

The results of our tests of the dehydrogenation of n-butane and isobutane are listed in Table 1. Owing to the well-known difficulties [7, 8, 9] involved in determining the true contact time τ in circulating systems, the table also gives the actual quantity of the butanes put through per hour. The length of the run was governed by the rate of feed of the butanes, since the same quantity – 4.5 liters – was run through in each test; this did not include the butane run through in the first half-hour of each test. The contact time was calculated from the formula:

$$\tau = \frac{2 \cdot V_r \cdot \eta \cdot T_k \cdot 3600}{V_{mf} (2 + \alpha) \cdot T_p},$$

where τ is the nominal contact time in seconds; V_r is the total volume of the reaction zone in sq cm; η is the portion of the free volume taken up by the catalyst, equal to 0.5; V_{mf} is the mean volume of material flow under operating conditions, in sq cm; α is the extent of dehydrogenation, expressed as a fraction of unity; T_k is the temperature of the gas in the gasometer in degrees K; T_r is the temperature of the gas in the reaction zone, in degrees K.

The ratio of the quantity of butylenes produced to the quantity of butane put through was taken as the extent of dehydrogenation. In view of the fact that the gas volume in the gasometer was measured to the nearest 10 ml, while the concentrations of butylene and isobutylene were measured with an accuracy of about 0.2%, the maximum relative error in determining the per cent dehydrogenation was 3-5%.

Inspection of Table 2 shows that the percentage of hydrogen in the reaction products is out of line with their butylene content. The discrepancy ranges from +22% to -12% when expressed as the ratio of the difference between the overall concentration of the butylenes and the isobutylene [$\sum C_4H_8$] and the hydrogen concentration to the $\sum C_4H_8$, multiplied by 100. In our opinion, this discrepancy cannot be explained by errors in analyses or in the experimental procedure. During the runs we observed the evolution of water, as a rule, at the T-joint located at the reactor outlet. This circumstance, together with the presence of small amounts of carbon dioxide in the reaction products, led us to conclude that the chromic oxide might be reduced principally by the hydrogen, but also to a minute degree by the gaseous hydrocarbons, during the process of dehydrogenation. But then less hydrogen should be exhausted than required by the buty-

TABLE 1

Results of Dehydrogenating n-Butane and Isobutane at Atmospheric Pressure with a Chrome Catalyst

Test No	Variables: Temperature (°C)	Volumetric feed rate, l/l cat. hr.	Rate of feed to reactor, l/hr.	Contact time, in sec.	Composition of the gaseous reaction products, per cent by volume: $n\text{-}C_4H_8$	$iso\text{-}C_4H_8$	H_2	$\sum C_4H_{10}$	"III" fraction	CO_2	Per cent dehydrogenation	Excess of deficiency of hydrogen, per cent	Per cent isomerization
					n-Butane								
4	502	205	3.07	3.25	6.9	1.5	8.8	82.5	–	0.3	9.3	- 4.8	17.9
5	503	196	2.94	3.24	8.2	0.5	8.0	83.0	–	0.3	9.6	+ 8.1	5.8
6	553	591	8.88	0.98	14.2	1.9	19.5	63.5	0.7	0.2	20.6	-21.1	11.2
7	553	454	6.80	1.22	19.7	2.7	25.1	52.1	1.0	0.4	30.5	+12.0	12.0[a]
8	553	354	5.30	1.51	23.2	4.6	26.7	44.1	1.0	0.4	38.5	+ 3.9	16.5
9	553	210	3.15	2.50	25.1	2.9	30.2	40.0[c]	1.3	0.5	41.3	- 7.9	10.3[b]
					Isobutane								
14	496	175	2.63	3.70	1.8	8.7	10.7	78.8	–	–	11.8	- 1.9	17.1
15	519	171	2.56	3.62	2.0	12.1	11.0	75.0	–	–	15.8	+22.0	14.2
16	553	591	8.88	1.00	1.4	11.6	14.1	72.2	0.6	0.1	15.9	- 8.5	10.8
18	553	382	5.74	1.49	2.8	17.6	16.3	61.8	1.1	0.4	24.8	+20.0	13.7
17	553	324	4.86	1.76	2.4	19.5	20.0	57.0	0.8	0.3	27.8	+ 8.7	10.9
13	553	181	2.72	3.06	3.8	21.1	23.5	50.4[d]	1.1	0.1	33.1	+ 5.6	15.2

Notes: a) Bloch and Schaad [4]: v = 415; time = 0.17 h; % isomerization = 7.5; conversion = 21.8%.
b) Bloch and Schaad [4]: v = 212; time = 0.30 h; % isomerization = 8.5; conversion = 28.2%.
c) Including 2% $iso\text{-}C_4H_{10}$.
d) Including 2.5% $n\text{-}C_4H_{10}$

TABLE 2

Isomerizing Action of a Chrome Catalyst at 553°

	n-Butane (Test 9)	Isobutane (Test 13)
Contact time, seconds	2.50	3.06
Per cent conversion	44.3	36.4
Per cent dehydrogenation	41.3	33.1
Yield, based on the converted initial product:		
Isobutane	6.8	–
Isobutylene	9.7	77.2
n-Butane	–	9.1
n-Butylene	83.5	13.7
Per cent isomerization	10.3	15.2

lenes, whereas in many runs we found an excess of hydrogen. Zelinsky, Bogdanova, and Shcheglova made a similar observation [10, 11] when they dehydrogenated butylenes to butadiene with a chrome catalyst, and attributed it to the decomposition

of the butylenes and the butadiene into carbon, methane, and hydrogen.

We were unable to find any methane in the products of butane dehydrogenation. Apparently the metallic chromium catalyzes the decomposition of the butylenes (or butanes) into carbon and hydrogen, which may be due to the formation of solutions of carbon in the chromium. We might mention that the formation of hydrogen in a larger quantity than called for by the dehydrogenation process has also been observed by us [12] in the aromatization of n-heptane, iso-octane, and some other hydrocarbons with a chrome catalyst. The fact that both an "excess" and a "deficiency" of hydrogen occurred in various runs is attributable, it seems, to the fact that the hydrocarbons are either oxidized or decomposed, depending upon the extent to which the properties of the catalyst were restored by regeneration and activation.

In view of the presence of isobutylene in the exhaust gases of the dehydrogenation of n-butane, we have calculated the per cent isomerization for all the tests. The per cent isomerization was calculated as the ratio of the concentration of isobutylene or of the n-butylenes to the overall concentration of the butylenes and the isobutylene. The per cent isomerization was calculated in the same way in the paper by Bloch and Schaad cited above [4]; hence, we can compare the isomerizing ability of the "dehydro-isomerizing catalyst" we used with that of the ordinary industrial chrome catalyst. The figures listed in Table 1 indicate that the per cent isomerization varied from 5.8 to 17.9% under our experimental conditions. We were unable to derive any regularity of behavior in the variation of the per cent isomerization with the temperature or the contact time in the tests we ran, since, although the limit of accuracy of 0.2% in determining the concentration of isobutylene or the butylenes was quite permissible for absorption analysis, the maximum relative error might go as high as 50% in individual runs, while it amounted to some 15 to 20% for most runs.

The figures listed in Table 2 are evidence of the appreciable isomerizing properties of the chrome catalyst prepared by simultaneously precipitating chrome and aluminum oxides in the isomerization of butylenes to isobutylene and of n-butane to isobutane.

A comparison of the typical chrome catalyst tested by us with the "dehydro-isomerizing" catalyst mixtures tested by Bloch and Schaad [4], cited in Table 1, indicates that chromic oxide on alumina is as good a "dehydro-isomerizer" as the cited catalyst mixtures. Parallel inspection of our findings, listed in Table 1, with those of Bloch and Schaad, cited in their paper [4], shows that mixing an aluminosilicate catalyst with a chrome catalyst in practice promotes a considerable increase in cracking reactions without increasing the isomerizing ability of the chrome catalyst.

Further research is required to tell whether the n-butane (Test 13) and the isobutane (Test 9) are primary or secondary conversion products of the initial hydrocarbon used in the test. One of the present authors has already reported on the isomerizing properties of chrome catalysts for 2,2,4-trimethylpentane and 2,3,3-trimethylbutene-1 and has suggested a possible way of effecting this isomerization via a three-membered ring [13, 14, 15]. At the same time as our publications, papers by Herrington and Rideal [16] were published, followed somewhat later by a paper by Raik [17], in which the formation of p-xylene from 2,2,4-trimethylpentene with a chrome catalyst was attributed to the formation of a five-membered ring which was converted into a six-membered ring at the instant of its formation (according to Raik). All the transformations described in the Herrington and Rideal papers are fully explained by the intermediate formation of a three-membered ring. The partial isomerization of isobutane and of n-butane during their dehydrogenation cannot be attributed to the formation of five-membered rings. As we see it, it is more than doubtful that the

pattern of the isomerizing ability of a chrome catalyst, suggested by us for the butanes does not apply to hydrocarbons of higher molecular weight, but is replaced by an ability to close a five-membered ring.

In working up the results of our observations we found that the variation of the per cent dehydrogenation with contact time is given by an equation that has been proposed, independently, it seems, by Academician Kolmogorov [22], Burlakov [18], Kazeev [19], and Erofeev [21], which we employed in a somewhat modified form:

$$\ln\left(\frac{D}{D-M}\right) = a\,\tau^{b}, \qquad (I)$$

where D is the maximum per cent dehydrogenation attainable in practice; M is the per cent dehydrogenation for a contact time at which the maximum dehydrogenation is not yet attained; τ is the contact time; a is a constant characterizing the velocity level of the reactions, and b is a constant indicating the reaction type.

It was found that at 553° the variation of the per cent dehydrogenation with the contact time is described by Equation (II) for n-butane and by Equation (III) for isobutane:

$$\ln\left(\frac{41.2}{41.2-M}\right) = 0.705\cdot\tau^{2.83}, \qquad (II)$$

$$\ln\left(\frac{33.1}{33.1-M}\right) = 0.698\cdot\tau^{1.59}. \qquad (III)$$

where M is expressed in per cent and τ in seconds.

The variation of the dehydrogenation rate $v = \frac{dM}{d\tau}$ with contact time is given by Equation (IV) for n-butane, while the rate of dehydrogenation of isobutane is given by Equation (V).

$$v_{n\text{-}C_4H_{10}} = [41.2 - M]\cdot 0.705\cdot 2.83\cdot\tau^{1.83}, \qquad (IV)$$

$$v_{iso\text{-}C_4H_{10}} = [33.1 - M]\cdot 0.698\cdot 1.59\cdot\tau^{0.59}. \qquad (V)$$

Inspection of these equations and of the respective curves in Fig. 1 indicates that at 553° the dehydrogenation of the butanes with a chrome catalyst involves an induction period and, hence, cannot be described by an equation of classical kinetics. At this temperature the dehydrogenation rate of the butanes is a maximum at a contact time $\tau_{max} = \left[\frac{(b-1)}{a\cdot b}\right]^{1/b}$. Substituting the respective values for a and b from Equations (II) and (III), we get τ_{max} = 0.98 seconds for n-butane and 0.67 seconds for isobutane at 553°.

We used the data of Taker, Folkins, and Muller [20] to calculate the equilibrium per cent dehydrogenation of n-butane and isobutane as a function of temperature, the respective figures being 40 and 61% for our temperature of 553° (Fig. 2). It follows that the value of the parameter D in Equation (II) is close to the equilibrium per cent dehydrogenation of n-butane, while the value of the parameter D in Equation (III) is about one-half of the equilibrium per cent dehydrogenation of isobutane.

In conclusion, we may point out that our results for the induction period differ from the findings of Grosse and Ipatieff [23], whose paper is often

cited. This paper indicates that there is no induction period in the dehydrogenation of the butanes.

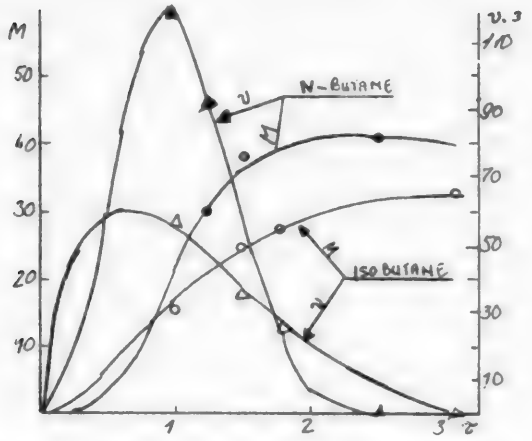

Fig. 1. Variation of the per cent (M) and the rate (v) of dehydrogenation with contact time. The curves have been plotted from Equations II-V.

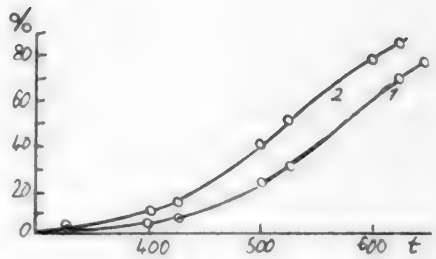

Fig. 2. Ratio of the percent dehydrogenation of n-butane (1) and isobutane (2) with variations of of temperature.

SUMMARY

1. Tests have been run on dehydrogenating n-butane and isobutane at the temperatures of approximately 500, 520, and 550° and at contact times ranging from 1.2 to 3 7 seconds, over a chromium catalyst prepared by simultaneously precipitating aluminum and chrome hydroxides. The experimental results indicate that the chrome catalyst used in the tests possesses considerable isomerizing ability

2. When the butanes are dehydrogenated with a chrome catalyst, the oxides are reduced and the butanes are decomposed into carbon and hydrogen, i.e., the catalyst is simultaneously activated and poisoned, which is responsible for the discrepancy between the percentage of hydrogen in the reaction products and the percentages of the butylenes and isobutylene.

3. Equations are proposed for the variation of the per cent and rate of dehydrogenation of n-butane and isobutane with contact time (for the temperature of 553°). The dehydrogenation has an induction period at this temperature.

4. The isomerizing ability of a chrome catalyst, as manifested in the dehydrogenation of the butanes and the presence of di-isobutylene [14, 15] in the products of the aromatization of 2,2,4-trimethylpentane, effected with the same chrome catalyst, render the aromatization equations proposed by Herrington and Rideal [16] and by Raik [17] highly dubious.

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Received July 2, 1952.

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THE ISOMERIZATION OF METHYLPHENYLETHYNYLCARBINOL IN AN ACID MEDIUM

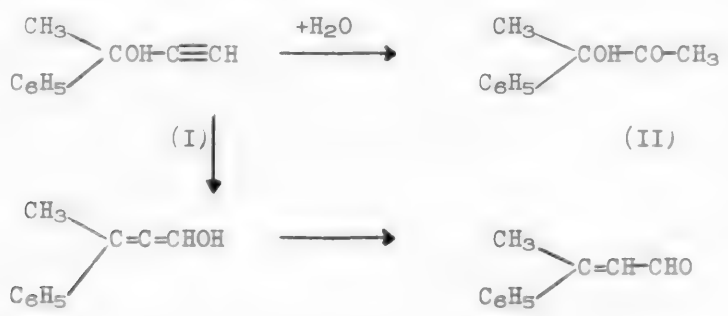
E.D.Venus-Danilova, A.P.Ivanov, and I.I.Martynov.

Methylphenylacetylcarbinol (1-phenylbutanol-2-one-1) (II) was required as the initial substance for the synthesis of acetylenic pinacols. There is an assertion in the literature [1] that this ketol can be obtained by hydrolysis of the corresponding hydrazone in the presence of benzaldehyde, the hydrazone being prepared by reacting the diacetyl hydrazone with phenylmagnesium bromide. Since this reaction could not provide large quantities of the ketol we required, we chose M.G.Kucherov's method [2] of hydrating acetylenic compounds in the presence of mercury salts.

Numerous chemists have investigated the hydration of tertiary acetylenic alcohols with mercury salts [3].

In hydrating methylphenylethynylcarbinol (I) with mercuric oxide and sulfuric acid we noticed that in addition to the expected ketol-methylphenylacetylcarbinol (II) we secured a low-boiling product that reacted with fuchsine sulfurous acid and with ammoniacal silver nitrate and yielded a semicarbazone The latter exhibited a depression of the melting point when mixed with acetophenone semicarbazone or with the semicarbazone of methylphenylacetylcarbinol, it being the semicarbazone of β-methylcinnamic aldehyde (IV) [4].

The formation of β-methylcinnamic aldehyde from methylphenylacetylcarbinol may be due to isomerization of the acetylenic alcohol in an acetylene-allene rearrangement, yielding the intermediate unstable hydroxyallene (III), which, as the enolic form of β-methylcinnamic aldehyde, is converted into the latter unsaturated aldehyde:



Rupe and his co-workers [5] were the first to describe the isomerization of acetylenic alcohols of the $RR_1COH-C\equiv CH$ type into unsaturated aldehydes by heating them with 80% formic acid, especially the conversion of methylphenylethynylcarbinol into β-methylcinnamic aldehyde (2% yield) [4]. The course of this conversion was traced as the successive addition and splitting out of water in the acetylenic alcohol [6].

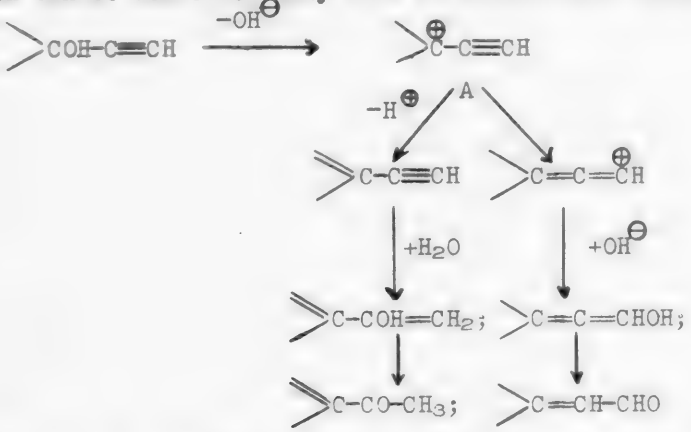
Further study of this reaction for various acetylenic alcohols yielded contradictory results, since in some cases unsaturated ketones were secured instead

of unsaturated aldehydes [7]. Some foreign chemists therefore were very skeptical of Rupe's findings, believing that nothing but unsaturated ketones were formed in all reactions of this sort [8].

In recent years American chemists [9,10,11] have made a thorough study of the isomerization of acetylenic alcohols and of the possible intermediate products of their transormations (ene-yne hydrocarbons) when acted upon by phthalic anhydride and phosphoric and sulfuric acids as well as by formic acid, finding that unsaturated aldehydes and sometimes acetylenic-ethylenic hydrocarbons are formed in addition to unsaturated ketones.

In evaluating the mechanism involved in the isomerization of acetylenic alcohols [10] they assume that a carbonium ion (A) is formed, which may change in two ways, yielding an aldehyde or a ketone, as indicated below.

The securing of nothing by cinnamic aldehyde [10] when phenylethynlcarbinol was reacted with 30% sulfuric acid confirms the reaction sequence outlined, since the carbonium ion can be converted only into an unsaturated aldehyde in this case.



The results of our experiments indicated that methylphenylethynylcarbinol is isomerized to β-methylcinnamic aldehyde when sulfuric acid is present. This fact, together with the papers by the chemists referred to [9,10,11], bears out the correctness of Rupe's researches, in which ethylenic aldehydes were found among the products of the isomerization of acetylenic alcohols, though this does not, of course, exclude the possibility of a ketone being formed at the same time. The parallel formation of an aldehyde and a ketone in varying proportions in this reaction must be indirectly related to the isomerization of aldehydes into ketones and to the formation of aldehydes and ketones when α-glycols are dehydrated [12].

EXPERIMENTAL

1. Synthesis of methylphenylethynylcarbinol. This alcohol was synthesized by the V.K.Teterin and A.P.Ivanov method [13], involving the simultaneous action of solutions of acetophenone and absolute alcohol in absolute ether upon diacetylene-magnesium dibromide. The organomagnesium compound was decomposed in the usual manner with water, the acetylenic alcohol being extracted with warm petroleum ether from the mixture of the alcohol with the acetylenic γ-glycol, the petroleum ether driven off, and the acetylenic alochol distilled with steam. When distillation was run at an extremely slow rate and strong chilling was employed, the alcohol solidified in the condenser, being secured in a highly pure state. This enabled us to reocver about 2/3 of the resultant alcohol, the remainder being recovered from the distillate by salting out with potash and extracting with ether. The yield of alcohol with a m.p. of 48.5 -49.5° varied from 29.5 to 31% of the theoretical, based on the acetophenone used for the reaction.

The yield of the acetylenic alcohol was always paralleled by the formation of symdimethyldiphenylbutynediol, its yield being some 36-42% of the theoretical.

2. Hydration of methylphenylethynylcarbinol. The carbinol was hydrated in an acetic acid solution with mercuric acetate, as in the hydration of phenylpropiolic alcohol [14]; it was also hydrated with dilute sulfuric acid and mercuric oxide in a water-alcohol medium. The results obtained by the first method were very poor, owing to the high tarring, satisfactory results being obtained by the second method. Six tests were run in all: two with mercuric acetate and four with mercuric oxide.

Tests with mercuric acetate. A solution of 4 g of methylphenylethynylcarbinol in 20 ml of 60% acetic acid was poured into a solution of 3.5 g of mercuric acetate in 30 ml of acetic acid. A flocculent white precipitate was thrown down at once, dissolving when the mixture was heated for two hours over a boiling water bath. The reaction products were steam-distilled, the distillate being saturated with soda and extracted with ether. After the extract had been desiccated with sodium sulfate and the ether had been driven off, the residue crystallized. The crystals were filtered out of the negligible quantity of liquid on a porous plate. This yielded 2.2 g of crystals that had a m.p. of 48-49° and constituted the initial acetylenic alcohol. A few drops of liquid were recovered; they reacted with fuchsine sulfurous acid, ammoniacal silver nitrate, and a solution of semicarbazide. The liquid was not subjected to further analysis because of the minute quantity available. An appreciable percentage of tar was left behind in the distilling flask after the volatile products had been distilled with steam.

Tests with mercuric oxide. A solution of 4 g of methylphenylethynylcarbinol in 20 ml of ethyl alcohol was poured into 2 g of mercuric oxide in 100 ml of (1.7) dilute sulfuric acid. A white flocculent precipitate was thrown down at once. The precipitate gradually dissolved when the mixture was heated for three hours over a boiling water bath with vigorous stirring. The reaction products were distilled with steam, the distillate being saturated with potash, extracted with ether, desiccated with sodium sulfate, and redistilled at 7 mm after the ether had been driven off:

I. B.p. 85-90°, 0.8 g. II. B.p. 90-103°, 0.3 g.
III. B.p. 103-104°, 1.2 g. Residue: 0.6 g of tar.

When the hydration test was repeated, the quantity of sulfuric acid was diminished, 60 ml of sulfuric acid being used for 4 g of the acetylenic alcohol, and the heating time was shortened (2 hours instead of 3). Distillation at reduced pressure (5mm) yielded 0.6 g of a substance with a b.p. of 76-77° and 1.5 g of a substance with a b.p. of 96-98°. In this second run we also noted the formation of some tar, both after steam distillation and after vacuum distillation.

Five hydration tests, using a total of 20 g of methylphenylethynylcarbinol, yielded 2.9 g of a substance with a b.p. of 76-77° at 5 mm and 7.0 g of a substance with a b.p. of 96-98°. The latter yielded a semicarbazone with a m.p. of 182-183°, which settled out of dilute alcohol as a fine powder. The literature gives a m.p. of 126-127° at 12 mm and a semicarbazone with a m.p. of 183-184° for methylphenylacetylcarbinol [15].

Analysis of the semicarbazone with a m.p. of 182-183°: 0.1002 g substance: 0.2186 g CO_2; 0.0631 g H_2O; 0.0902 g substance: 14.9 ml N_2 (15°, 762 mm). Found %: C 59.50; H 7.00; N 19.31. $C_{11}H_{15}O_2N_3$. Calculated %: C 59.73; H.6.79; N 19.00

The yield of the methylphenylacetylcarbinol was 28.8% of the theoretical.

The substance with a m.p. of 76-77° at 5 mm reacted with ammoniacal silver nitrate and yielded a semicarbazone that had a m.p. of 198-199° after repeated

recrystallization from aqueous alcohol and exhibited a depression of the melting point when mixed with acetophenone semicarbazone or with the semicarbazone of methylphenylacetylcarbinol. The yield of the β-methylcinnamic aldehyde was 14.5% of the theoretical. The b.p. of β-methylcinnamic aldehyde is given in the literature as 122-130° at 12 mm, while the m.p. of its semicarbazone is given as 201° [4].

The unsaturated aldehyde settled out very quickly from the mixture of the β-methylcinnamic aldehyde and the semicarbazone of methylphenylacetylcarbinol, so that it can be readily isolated from the semicarbazone of the ketol, which settles out much more slowly.

0.0903 g substance; 0.2158 g CO_2; 0.0538 g H_2O; 0.0904 g substance; 16.1 ml N_2 (18°, 763 mm). Found %; C 65.20; H 6.62; N 20.95. $C_{11}H_{13}ON_3$. Calculated %; C 65.60; H 6.40; N 20.75.

Attempts to secure the silver salt of β-methylcinnamic acid from the β-methylcinnamic aldehyde by oxidizing the aldehyde with silver oxide met with failure. When we heated the aldehyde in aqueous alcohol with freshly precipitated silver oxide, we got a very good silver mirror, but the silver salt secured was all acetate. The neutral oxidation products contained acetophenone, identified as in semicarbazone with a m.p. of 200-201°. It must be assumed that the oxidation of the unsaturated aldehyde was paralleled by hydration and the cleavage of the double bond. The silver salt of β-methylcinnamic acid has been described in the literature [15], but it was prepared in a double decomposition reaction between the sodium salt of β-methylcinnamic acid and silver nitrate.

SUMMARY

1. Hydration of methylphenylethynylcarbinol with mercuric oxide and dilute sulfuric acid yielded 14.5% of β-methylcinnamic aldehyde in addition to the normal hydration product - 28.8% of methylphenylacetylcarbinol.

2. The unsaturated aldehyde is formed from the acetylenic alcohol as the result of an anionotropic acetylene-allene rearrangement via the enolic form of the unsaturated aldehyde.

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Received December 26, 1949.

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ACETYLENE-ALLENE REARRANGEMENTS

IV. AN IONIC THEORY OF ACETYLENE-ALLENE REARRANGEMENTS

A. N. Pudovik

A survey of the experimental researches on acetylene-allene rearrangements performed by now indicates that this interesting field of isomeric transformations has been explored much less extensively or intensively than, say, the related field of allyl rearrangements. The reason for this is apparently that acetylene-allene rearrangements were discovered fairly recently, the attention of chemists having been drawn to this research field chiefly by the researches of Academician A E.Favorsky and his pupils: T.A.Favorskaya, A.I.Zakharova, I.A.Favorskaya, and others in the course of the past 15 years. The original concepts of the mechanism involved in acetylene-allene rearrangements were elaborated by Meyer and Schuster in 1922 [1]. They assumed that the isomerization of acetylenic carbinols to unsaturated ketones involved the shift of the hydroxyl group from the α-to the γ-carbon atom, resulting in the formation of intermediate carbinols of the allene type. They thought it was not impossible, however, that the reaction also takes a different course, involving the addition of a molecule of water to the acetylenic alcohol, followed by its being split out, though along different lines.

Subsequently, the latter view was adopted and developed by Rupe [2] to explain the isomerization of acetylenic carbinols to unsaturated aldehydes. The value of these concepts was rendered largely problematical after several scientists [3] had shown that when tertiary acetylenic carbinols are isomerized, it is the unsaturated ketones, rather than unsaturated aldehydes, that are formed in most instances.

We are indebted to the research of Academician A.E.Favorsky and his school for further progress in the evolution of our concepts of the mechanisms involved in acetylene-allene rearrangements. In 1935 A.E.Favorsky and T.A. Favorskaya [4] discovered and subsequently made an extensive study of an acetylene-allene-diene rearrangement in acetylenic halogen derivatives. In 1937 A.E.Favorsky advanced the theory of intramolecular rearrangements as an explanation of these and similar transformations [5]. This theory was of great significance in the development of organic chemistry, since it made it possible to generalize and systematize a vast amount of factual data on all sorts of transformations of unsaturated hydrocarbons, halogen derivatives, and the like. One weak point of this theory is the fact that though it correctly describes the nature of the various transformations, " it does not explain the nature or the cause of the phenomena described" [6].

The study of allyl-and acetylene-allene rearrangements that I have been making for the past few years has led me to conclude that both of these types of rearrangements are closely alike in their nature and the way in which they occur. In the isomerization, for instance, of acetylenic halides to allene halides, the halogen atom is shifted from the α - to the γ-carbon atom while the triple bond's electron pair is shifted from the β, γ - position to the α-β

position, producing an allene system. Similar displacements take place in allyl rearrangements.

In the nucleophilic substitution of any other negatively charged anion for a halogen atom in compounds of the acetylenic halide type, as well as when a halogen atom attached to a saturated carbon atom, or in unsaturated allylic systems is replaced, the reaction may be of two kinds; bimolecular and monomolecular.

Ingold and Hughes [7] investigated the ratio of bimolecular to monomolecular mechanisms in substitution reactions in the following series: CH_3X, CH_3CH_2X, $(CH_3)_2CHX$, and $(CH_3)_3CX$ and concluded that the bimolecular mechanism ought to yield progresively to the monomolecular mechanism, owing to an increase in the induction effect produced by the allyl groups. As a matter of fact, research on the kinetics of hydrolysis reactions has shown that this change in the mechanism applies to isopropyl compounds, the hydrolysis of tert-butyl chloride being exclusively monomolecular.

The conclusions I reached in my previous researches on the mechanism involved in substitution reactions in isomeric allyl halogen compounds agree fully with the conclusions set forth above. In most of the reactions studied, the primary allyl halogen compounds react solely or chiefly bimolecularly, yielding a normal product without any rearrangement, whereas secondary allyl halogen compounds react solely or chiefly monomolecularly, with a rearrangement, yielding either a mixture of the two isomers or a product whose structure is that of the primary allyl derivative.

The findings on the replacement of the halogen atom in saturated compounds and in allyl isomers serve as a basis for several conclusions regarding the nature of substitution in acetylenic halogen derivatives as well. The structure of the acetylenic halides investigated is that of tertiary halogen derivatives, and the monomolecular mechanism should predominate in substitution reactions involving them as well as tertiary alkyl halides.

The tendency toward monomolecular substitution in tertiary acetylenic chlorides ought to be greater than in secondary allyl halide isomers and somewhat less than, say, in tert-butyl chloride, inasmuch as the acetylene group attracts electrons, its action tending to diminish the electron density around the central carbon atom.

In allyl rearrangements, as in many others, we have a very simple and reliable criterion of whether a reaction is monomolecular, based on a comparison of the ratio between the isomeric compounds secured from the two allyl halide isomers In acetylene-allene rearrangements the problem of proving the reality of the monomolecular mechanism is somewhat more complicated in that in some cases it is only with the acetylenic chlorides, which possess a mobile halogen atom, that a substitution reaction can be effected with most reagents under the usual reaction conditions. As a rule, the halogen atom attached to the carbon atom linked by a double bond in allyl isomers is either not at all active or only very slightly so. Because of this, in our study of acetylene-allene rearrangements we must most often confine ourselves to the reactions of acetylenic chlorides which does not always allow us to establish a complete picture of the substitution mechanism and of the rearrangements involved therein. Nonetheless, whenever a reaction results in the formation of an isomeric product from acetylene or allene halogen derivatives, we may be sure that the reaction is a monomolecular one.[1])

The reactions between silver acetate and dimethylethynylchloromethane, investigated by A.I.Zakharova [8] for example, as well as the reactions between acetylenic chlorides and organomagnesium compounds, described [2]) by her in 1947 [9] and by L.Mukhamedova and the present author some years later [10], evidently are monomolecular in so far as the formation of allene derivatives are concerned.

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[1]) and [2]) – See following page.

The acetylene-allene rearrangement of acetylene chlorides that occur when copper sesquichloride is present, investigated by T.A.Favorskaya [11], may be satisfactorily explained by means of a similar pattern, proposed by me to explain the catalytic isomerization of allyl halide isomers when acted upon by metal halides [12].

As I have shown in the present paper, the catalytic isomerization of an acetylenic chloride occurs whether hydrochloric acid is present or not, though the rate of isomerization is much lower when no acid is present. As the experimental curves reproduced in the adjoining drawing show, the equilibrium is nearly entirely displaced toward the allenic chloride. Evidently, of the two isomeric chlorides, the allenic chloride is more stable thermodynamically. Curve I represents the isomerization of the chloride with mercurous chloride present, Curve II representing isomerization with cupric bromide. Curve III isomerization with partially oxidized cuprous chloride, and IV isomerization with freshly prepared cuprous chloride. The allenic chloride underwent practically no isomerization (V) when cuprous iodide was present.

The further isomerization of the allenic chloride to a diene chloride, discovered by T.A Favorskaya [13], which also takes place in the presence of cuprous chloride, may be regarded as an isomeric transformation of the prototropic type, following a monomolecular pattern and due to the tendency of the allene chloride, which possesses a cumulative system of double bonds, to change into a thermodynamically more stable diene chloride with a conjugated system of double bonds.

The hydrolysis of 1-chloro-3-methylbutadiene-1,2, explored by T.A.Favorskaya [13], is evidently monomolecular as well, in so far as the formation of an acetylenic alcohol is concerned, as is the reaction of dimethylethynylchloromethane with phosphorous esters, explored by me [14].

The greates difficulties are encountered in the theoretical interpretation of such reactions as, for instance, the hydrolysis and alcoholysis of acetylenic chlorides, which result in the formation of acetylenic alcohols and ethers of similar structure.

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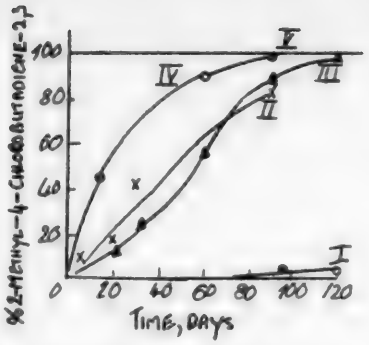
[1]) Research upon the reactions of acetylenic halogen compounds with neutral nucleophilic reagents, such as the amines, may introduce a restriction into this conclusion. As Young and his co-workers have recently shown [JACS 73, 1080 (1951)], amines react largely bimolecularly with secondary allyl halogen compounds it seems. At the present time we know of no reactions of acetylenic halogen compounds that occur via an S_{N2} mechanism, in view of the structural factors involved, the probability of their occurrence should be much less than that of allyl halogen compounds, for which they are apparently rare enough.

[2]) In this paper A.I.Zakharova for the first time advances the a priori hypothesis that a carbonium ion may be formed during the reaction of an acetylenic chloride and an organomagnesium compound.

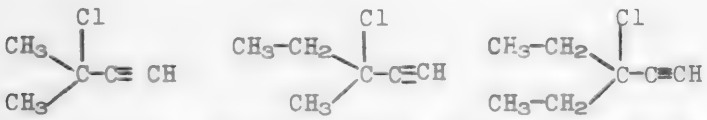
The results give us no basis for judging how these reactions occur, inasmuch as products whose structure resembles that of the initial substance may be formed monomolecularly or bimolecularly or by a combination of the two simultaneously.



To solve the problem of the mechanism involved in these reactions I made a study of the kinetics of the hydrolysis of dimethylethynylchloromethane and of methylethylethynylchloromethane in water-alcohol and acetone solutions. Investigation of the hydrolysis of dimethylethynylchloromethane in 50% ethyl alcohol and 50% aqueous acetone at 35° indicated that the velocity constants of these reactions, as calculated from the equation for a first-order reaction, suffer practically no change with time. This is conclusive proof that the reactions are monomolecular.

It is worthy of note that, under identical experimental condtions, the hydrolysis of methylethylethynylchloromethane is slower [$\underline{K}$ = 0.0145] than that of dimethylethynylchloromethane [$\underline{K}$=0.0220].

A similar phenomenon was observed by T.A.Favorskaya, A.I.Zakharova, and I.A. Favorskaya [11] in their research on the isomerization of various acetylenic chlorides to allenic chlorides in the presence of cuprous chloride, ammonium chloride, and hydrochloric acid. Their study of the composition of the reaction products indicated that the isomerization rate diminished from left to right in the following order:

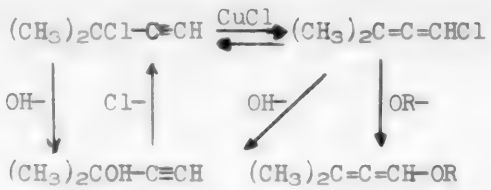


An increase in the induction effect of the alkyl groups in the foregoing series of compounds as ethyl groups are accumulated within them should, it would seem, increase the mobility of the halogen atom and facilitate its removal as an anion during the monomolecular isomerization process. The actual order in which the hydrolysis and isomerization rates increase is exactly opposite. The decisive factor affecting the decrease in the rates of hydrolysis and isomerization in this series is, apparently, the decrease in the conjugation effect, due to a change in the structure of the radicals comprising the chlorides.

A study of the kinetics of the hydrolysis of the allene chloride 2-methyl-4-chlorobutadiene-2,3 in water-alcohol solutions of various compositions indicated that its velocity varied quite considerably with time. This is due to the fact that in the hydrolysis of the allene chloride the formation of an acetylenic alcohol, which was a monomolecular reaction, was paralleled by the production of a number of other products, the manner of their formation not being wholly understood as yet.

As for the reasons for the formation of products with the structure of the initial chlorides in the monomolecular process involved in the hydrolysis and alcoholysis of tertiary acetylenic chlorides, here, as in the tertiary chlorides of the allyl type, it is the kinetic factors that apparently are decisive. The reactions begin with the formation of products that possess kinetic advantages though they

are less stable thermodynamically, in amounts that far exceed their content in the state of equilibrium.



EXPERIMENTAL

Kinetics of the hydrolysis of dimethylethynylchloromethane and 2-methyl-4-chlorobutadiene-2,3. The dimethylethynylchloromethane and the 2-methyl-4-chlorobutadiene-2,3 were hydrolyzed in water-alcohol and water-acetone solutions. About 200 ml of the previously prepared alcohol or acetone solution of the specified concentration was poured into a 250-ml measuring flask, which was then placed in a thermostat, the temperature of which was controlled to within ±0.1°. After the flask contents had reached the thermostat's temperature (this took 30 minutes), a measured quantity of the chloride, plus the amount of the water-alcohol or water-acetone solution required to fill the flask to the mark, which had been kept for a long time in the thermostat, was added from a pipet. Samples of the solution, totaling 25 ml each time, were taken from the flask at specified intervals and immediately titrated with an aqueous solution of NaOH and phenolphthalein.

TABLE 1

Hydrolysis of Dimethylethynylchloromethane in a Water-Alcohol Solution

Test 1 50% alcohol. Temperature: 35° Weight of chloride: 1.5015 g; a = 58.6 ml N/40 NaOH. Time in minutes. K_1 = velocity constant for a monomolecular reaction.			Test 2 Alcohol 50%. Temperature: 30° Weight of chloride: 2.0721 g; a = 83.6 ml N/40 NaOH. Time in minutes. K_1 = velocity constant for a monomolecular reaction.		
t	x	K_1	t	x	K_1
32	4.05	0.00223	30	4.60	0.00187
45	5.70	0.00227	60	8.15	0.00171
60	7.45	0.00226	75	11.00	0.00188
75	9.00	0.00222	90	12.75	0.00183
90	10.45	0.00218	105	14.95	0.00187
120	13.25	0.00213	120	16.95	0.00189
180	18.95	0.00211	135	18.40	0.00184
			150	19.65	0.00179
	Mean . .	0.00220		Mean ..	0.00184

The hydrolysis constant was computed from the formula for a first-order reaction, in which t is the time in minutes; a is the initial concentration of the chloride in 25 ml of solution, expressed in the equivalent number of ml of a N/40 or N/200 alkali solution; and a - x is the chloride concentration in 25 ml of solution at time t, expressed in ml of a N/40 or N/200 alkali solution used in titrating 25 ml of the solution after the lapse of time t [Tables 1, 2, and 3].

TABLE 2

Hydrolysis of Dimethylethynylchloromethane in a Water-Acetone Solution

Acetone 39.9%. Temperature: 35°. Weight of chloride: 1.5015 g; a = 293.0 ml N/200 NaOH. Time in minutes. K_1 = velocity constant for a monomolecular reaction.

t	x	K_1
90	32.0	0.00128
120	40.7	0.00124
150	54.6	0.00136
180	68.1	0.00146
210	73.6	0.00137
240	83.6	0.00137
270	85.8	0.00129
	Mean	0.00133

TABLE 3

Hydrolysis of 2-methyl-4-chlorobutadiene-2,3 in a Water-Alcohol Solution

Alcohol 50%. Temperature: 35°. Weight of chloride: 2.0721 g; a = 418 ml N/200 NaOH. Time in minutes. K_1 calculated from the equation for a monomolecular reaction.

t	x	K_1
60	6.2	0.000247
120	9.65	0.000195
180	11.30	0.000157
240	12.90	0.000131
300	16.40	0.000133
360	16.70	0.000113
420	18.30	0.000106
480	19.60	0.000100
540	20.10	0.000091

TABLE 4

Isomerization time, minutes	Isomerization of dimethylethynylchloromethane												Isomerization of 2-methyl-4-chlorobutadiene-2,3	
	Freshly prepared CuCl		Partially oxidized CuCl		$CuBr_2$		CuI		HgCl		$CrCl_3$			
	n_D^{20}	Isomerization %	n_D^{20}	Isomerization %	n_D^{20}	Isomerization %	n_D^{20}	Isomerization %	n_D^{20}	Isomerization %	n_D^{20}	Isomerization %	n_D^{20}	Isomerization %
2	1.4210	5.2					1.4203	4.0					1.4750	0.0
5			1.4230	8.8										
14	1.4430	43.8					1.4207	4.7	1.4180	0.0				
20			1.4280	17.5	1.4245	11.4			1.4180	0.0	1.4180	0.0		
30			1.4423	42.6	1.4320	24.5	1.4262	14.4	1.4180	0.0	1.4185	0.7	1.4750	0.0
60	1.4690	89.4	1.4500	56.1	1.4490	54.4	1.4610	75.4	1.4185	0.7	1.4190	1.7	1.4750	0.0
90	1.4740	98.2	1.4647	81.9	1.4680	87.7	1.4690	89.4	1.4190	1.7	1.4190	1.7	1.4750	0.0
120					1.4740	98.2			1.4203	4.0				

Besides the experiments cited, we also ran tests of the rate of hydrolysis of dimethylethynylchloromethane at higher temperatures. We found that under these conditions the constant calculated from the equation for monomolecular reactions had a very slight, but unvarying, tendency to diminish with time. As I see it, this is due to the fact that as the temperature is raised hydrolysis is accompanied by a perceptible addition reaction of the hydrogen chloride evolved during hydrolysis to the triple bond of the dimethylethynylchloroethane.

Isomerization of dimethylethynylchloromethane and 2-methyl-4-chlorobutadiene-2,3 with metal halides. The procedure I used for this resembled the one described

for isomerizing the isomeric alkoxychloropentenes [12]. The percent isomerization of the chlorides was calculated from the change in the refractive index of the reaction mixture. In most cases we measured the refractive index directly for the reaction solutions, only in some instances was the index measured after the insufficiently transparent solution had been distilled at a slight vacuum. We were unable to investigate the isomerization of dimethylethynylchloromethane with zinc salts, since the latter caused pronounced tarring of the chloride. We ran tests of the isomerization of dimethylethynylchloromethane with cuprous chloride.[1] All of these salts dissolved extremely slowly in the chloride, much of the salt remaining undissolved in the bottom of the flask after the completion of each test. We therefore were unable to study how the chlorides were isomerized at various concentrations of the salts. The results of our experiments on the isomerization of dimethylethynylchloromethane and 2-methyl-4-chlorobutadiene-2,3 are given in Table 4. The constants of the chlorides we used in these catalytic isomerization tests were as follows: dimethylethynylchloromethane b.p. 74-76°; n_D^{20} 1.4180; 2-methyl-4-chlorobutadiene-2,3: b.p. 41°/90 mm; n_D^{20} 1.4750

SUMMARY

1. A study of the kinetics involved has demonstrated that the hydrolysis of acetylenic chlorides is a monomolecular reaction.

2. The catalytic isomerization of dimethylethynylchloromethane with metal halides has been investigated.

3. An ionic theory is advanced for the mechanism of acetylene-allene rearrangements.

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Received June 15, 1949.

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[1]) Cupric bromide, cuprous iodide, mercurous chloride, and chromous chloride as well.

[2]) See Consultants Bureau English translation, p. 1603.

[3]) See Consultants Bureau English translation, p. 97.

[4]) See Consultants Bureau English translation, p. 1593.

RESEARCH OF UNSATURATED CYCLIC HYDROCARBONS AND THEIR HALOGEN DERIVATIVES

XI. THE MECHANISM OF COMBINED HALOGENATION AND DEHALOGENATION REACTIONS

N A. Domnin, V. A. Cherkasova, and S. N. Andreev

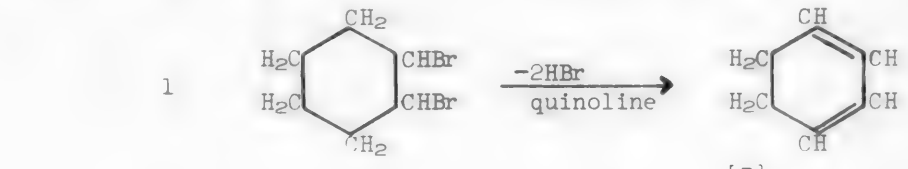
One of the essential properties of halogen derivatives of cyclohexane is their ability to change into aromatic compounds when heated with quinoline [1, 2, 3]. The first observations of transformations of this sort were made by Willstätter and Hatt [4], who found that the hydrocarbon mixture produced by reacting 1,2-dibromocyclohexane contained about 14% of benzene in addition to cyclohexadiene-1, 3 and cyclohexene. The authors isolated the benzene in the pure state and identified it rather completely.

Although this interesting transformation was known as far back as 1912, no new references to it appeared in the literature for a long time, until one of the present authors posed the problem of the mechanism involved in these transformations in 1946 [2]. At that time transformations of this sort were called combined halogenation-dehalogentation reactions and a pattern was suggested for these reactions [11].

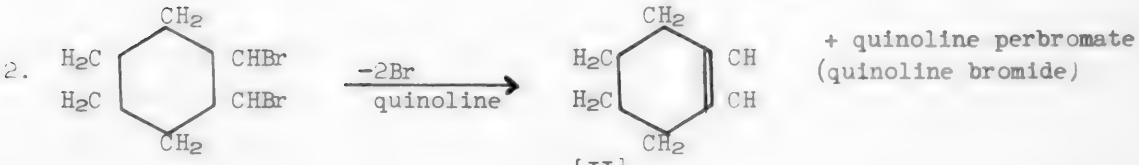
This pattern is based, first, upon the ability of quinoline to split elements of hydrobromic acid as well as two bromine atoms out of bromine derivatives of hydrocarbons; and, second, upon the inadequate stability of the addition products of bromine and quinoline and upon the ability of these compounds to yield up the added bromine molecule under certain conditions to molecules that can retain the bromine more firmly.

Whether the transformation of polyhalogenated derivatives of cyclohexane into aromatic compounds when they are heated with quinoline followed the proposed pattern was a matter of great theoretical interest. This is the topic of the present research.

1,2-Dibromocyclohexane was selected as the test subject for transformations of this type. Its conversion into an aromatic compound (benzene) when heated with quinoline, which was established by Willstätter and confirmed by our own researches, takes place as follows:



[I]



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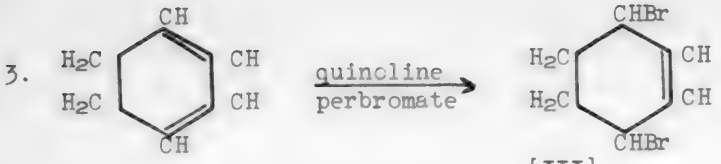
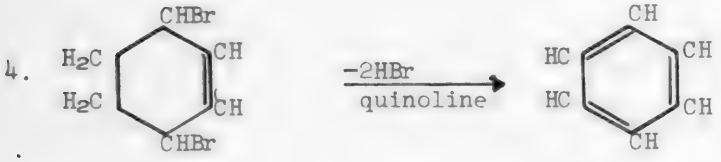


[III]



[IV]

Cyclohexadiene-1,3, the first component of the combined halogenation and dehalogenation reaction, was prepared by a preliminary Hoffmann-Damm synthesis [5]. The second reagent, quinoline perbromate (quinoline bromide), was prepared (i.e., the second stage was carried out) by reacting hexabromoethane with quinoline. A mixture of all the reagents used in the combined halogenation-dehalogenation reaction (cyclohexadiene-1,3, hexabromoethane, and quinoline) was heated to 110-140° over an oil bath for 2-3 hours in a small flask fitted with a reflux condenser, after which the volatile reaction product was driven off.

We were unable to employ the nitration method as a check or for a quantitative determination of the aromatic hydrocarbon formed, since several research workers have shown that the action of a nitrating acid upon homologs of cyclohexene and upon 1,3- and 1,4-cyclohexadienes results in the formation of nitro aromatic derivatives [6,7,8,9]. Our investigations also demonstrated that a toluene-free methylcyclohexadiene-1,3, prepared by reacting methyl-o-dibromocyclohexane with an anhydrous alkali, yields about 6% of dinitrotoluene when reacted with a nitrating acid. That is why we performed the qualitative and quantitative analysis of the reaction mixture for the aromatic hydrocarbon formed during the course of the reaction by means of absorption spectroscopy in the ultraviolet - the first use of this method to analyze the reaction products of combined halogenation-dehalogenation.

The reaction products were analyzed qualitatively and quantitatively by photographing the absorption spectra of their one per cent solutions in ethyl alcohol by the variable thickness method. Although the absorption band of cyclohexadiene-1,3 is superposed on the spectral absorption bands of benzene, qualitative and quantitative analysis of their mixture is quite feasible. The absorption band of cyclohexadiene-1,3 does not have a clearly marked maximum. The absorption band of benzene has a sharply defined fine structure, with maxima at 2425, 2485, 2540 and 2600 Å, which makes it possible to analyze the reaction product qualitatively for the presence of benzene and to measure the latter quantitatively in the mixture with cyclohexadiene-1,3 with an accuracy of ±10%.

The solution under test was placed in front of the slit in an ISP-22 quartz spectrograph, in a gold-plated cell of variable length, which made it possible to vary the layer thickness from zero to 10 mm with an accuracy of ±0.003 mm. A hydrogen lamp manufactured by the Etalon factory was used as a source of light providing a continous spectrum. The spectrograms were photographed on a diapositive plate with a sensitivity of 2° H and D. The exposure time for one spectrum was 1 minute. In the quantitative analysis of the mixture it is extremely important that the light

source be constant We determined, in a preliminary test of the operation of the "Etalon" hydrogen lamp that the voltage across its terminals did not fluctuate by more than 1-2% throughout an exposure, which enabled us to employ it without any stabilization

Benzene is detected qualitatively in a mixture with cyclohexadiene-1,3 by means of the appearance of the strongest absorption bands of benzene in the spectrogram against the background of the absorption band of cyclohexadiene-1,3. This method enabled us to detect the presence of benzene in a cyclohexadiene-1,3 mixture when its proportion in the mixture by weight was only 1:10.

We employed a calibration curve to analyze the mixture quantitatively for its percentage of benzene A series of standard solutions of benzene in ethyl alcohol (ranging from 1 to 0 01% of benzene by weight) was photographed by the variable length method, the exposures being 1 minute long. In the spectrogram of each standard solution, we chose the spectrum in which the eye first detected absorption at 2600 Å The lower the concentration of benzene, the greater the thickness of the critical layer corresponding to this standard solution spectrum The critical thicknesses of the standard solutions were laid off as ordinates on a graph, the corresponding concentrations being the abscissas. The plotted points were connected together, the resulting calibration curve being used for the series analysis of the mixtures for benzene.

The quantitative analysis comprised the following. the absorption spectra of a one per cent solution of the test mixture in ethyl alcohol was photographed by the variable thickness method; the critical thickness of the solution layer was found in the spectrogram; and the benzene concentration corresponding to this critical thickness was found on the calibration curve. The percentage error of the method was about ±10% of the resultant concentration of benzene in the reaction product.

The absorption spectrum of the product secured in the reaction of cyclohexadiene-1,3, hexabromoethane, and quinoline differed sharply from the absorption spectrum of the original cyclohexadiene-1,3, but coincided fully with the absorption spectrum of benzene, in the location of the absorption bands as well as in the distribution of intensities within them. It was determined visually that the benzene in the resultant product amounted to 90%. This transformation may be represented by Stages 3 and 4 in the reaction sequence set forth above.

To check whether the benzene was actually produced in a combined halogenation-dehalogenation reaction, rather than as the result of an irreversible Zelinsky catalysis, i e , a redistribution of the hydrogen among the cyclohexadiene-1,3 molecules in the presence of the quinoline, we heated equimolecular quantities of cyclohexadiene-1,3 and quinoline to 130-150° for 6 hours in a small flask fitted with a reflux condenser The constants of the distilled hydrocarbon were, however, the same as those of the initial cyclohexadiene-1,3. Nor was any benzene detected spectroscopically, i e , no Zelinsky irreversible catalysis occurs under these conditions.

To check whether benzene was formed directly in a reaction of the cyclohexadiene-1,3 with the hexabromoethane, we heated an equimolecular mixture of the two to 130-150° for 5 hours in a small flask fitted with a reflux condenser. No benzene was found in the distillate in this test either.

These tests showed that the benzene found in the product of the reaction of hexabromoethane, quinoline, and cyclohexadiene-1,3 could only be formed when all three reagents were present, i e , only in a combined halogenation-dehalogenation reaction.

The reaction of cyclohexadiene-1,3 with hexabromoethane and quinoline hydro-

bromide (instead of free quinoline) yielded a product containing about 30% benzene, which is evidence of the ability of this salt to detach bromine from the hexabromoethane molecule, yielding quinoline perbromate – an intermediate reaction product – while the cyclohexadiene-1,3 was brominated to dibromocyclohexene.

The fact that benzene is formed from cyclohexadiene-1,3 when the latter is reacted with hexabromoethane in the presence of quinoline or the latter's hydrobromide is confirmation of the first stage of the reaction sequence (the formation of a sixmembered ring with conjugated double bonds).

EXPERIMENTAL

Action of quinoline upon 1,2-dibromocyclohexane. 24.2 g of 1,2-dibromocyclohexane was cautiously added from a dropping funnel (avoiding any violent reaction) to 30 g of previously-heated quinoline in a Würtz flask. The distillate was washed with water, desiccated with calcium chloride and then with metallic sodium, and redistilled. The fraction with a b.p. of 80-81.3° (2.5 g) had a n_D^{19} 1.4686 and a bromine number of 165. The bromine number of cyclonexadiene-1,3 is 200 (calculated on the basis of the addition of two atoms of bromine to the cyclohexadiene-1,3 molecule). It was found spectroscopically that the resultant product contained 10-20% of benzene.

The combined halogenation-dehalogenation reaction. The following reagents were used in this reaction:

Cyclohexadiene-1,3, prepared by the Hoffmann-Damm method [5].

B.p. 79.5-81°; d_4^{20} 0.8394; n_D^{20} 1.4742; MR_D 26.79; bromine number 192.

Hexabromoethane, prepared by the Gustavson method [12].

B.p. 182-187° (with decomposition); % Br: 94.80, 95.48; M 461.7; calculated %: Br: 95.23, M 503.5.

Quinoline, prepared by the Skraup synthesis:

B.p. 94-94.5° (6.5-7 mm); $n_D^{20.5}$ 1.6232.

Experiment 1. 49 g of hexabromoethane was heated to 100-125° with 12.5 g of quinoline for 20 minutes in a small flask fitted with a reflux condenser. A peculiar crackling sound was audible during this process. When the bath temperature reached 135°, a few red spots appeared on the wall of the flask, and soon the flask contents were converted into a red crystalline mass that smelled strongly of bromine. After the reaction mass had cooled to room temperature, 7.7 g of cyclohexadiene-1,3 and 25 g of quinoline were added, and heating was continued for 2 hours (the red color disappearing); then a fraction with a b.p. of 83-135 (5.1 g) was distilled off. This distillate was washed with dilute H_2SO_4 and with water and desiccated with calcium chloride, after which it was distilled with metallic sodium. The 79-84° fraction (4.6 g) had a n_D^{18} 1.4889, and a bromine number of 67. Spectroscopic analysis indicated that the product contained some 70% of benzene. We carried out the next reaction without first heating the hexabromoethane with the quinoline, which possibly promoted the preliminary synthesis of quinoline perbromate.

Experiment 2. 5.2 g of cyclohexadiene-1,3, 38 g of hexabromoethane, and 5 g of quinoline were heated together to 100-110° for 1 hour 20 minutes in a small flask over an oil bath, fitted with a reflux condenser (here again we heard a peculiar crackling sound, which grew stronger when the reaction mixture was stirred). Then the mixture was heated to 130-145° for 40 minutes, which caused large quantities

of hydrogen bromide to be liberated. The flask's contents were cooled to 70°, 17 g of quinoline was added, and heating was continued for another 2 hours, after which a 70-200° fraction was distilled from the highly tarred mass. This fraction was washed with dilute sulfuric acid and desiccated, after which it was distilled with metallic sodium. The highly volatile fraction (2.2 g), which crystallized in a freezing mixture (snow and salt), had the following constants:

B.p. 80-82°; n_D^{18} 1.5020; d_4^{18} 0.8837; MR_D 26.05. $C_6H_6F_2$. calculated MR_D 26.31.

It was found spectroscopically that the end product contained 85-90% of benzene

Experiment 3. 16 g of quinoline hydrobromide was heated to 110-130° over an oil bath with 38.5 g of hexabromoethane in a small flask fitted with a reflux condenser, closed off with a stopper bearing a calcium chloride tube. After 20 to 30 minutes of heating (during which crackling was audible, faint at first, and then growing stronger), red crystals began to form, the contents of the flask soon turning into a red crystalline mass that smelled strongly of bromine. The color gradually disappeared when 2.6 g of cyclohexadiene-1,3 was added. After 20 minutes of heating, 10 g of quinoline was added, and heating was continued for another 20 minutes. The distilled highly-volatile fraction (1.1 g) was washed with water and desiccated with calcium chloride, after which it had a b.p. of 79.5-81° and a n_D^{18} 1.4820, and contained about 30% of benzene according to the spectroscopic findings.

SUMMARY

1. The method of absorption spectroscopy in the ultraviolet has been employed to establish that a mixture of products containing 10 to 20% of benzene is secured when 1,2-dibromocyclohexane is reacted with quinoline.

2. Reacting cyclohexadiene-1,3, hexabromoethane, and quinoline together yields a mixture of products that contains 85 to 90% of benzene.

3. Reacting cyclohexadiene-1,3, hexabromoethane, and quinoline hydrobromide together yields a mixture of products that contains about 30% of benzene.

4. It has been shown that the first stage in the conversion of polyhalogenated derivatives of cyclohexane into aromatic compounds by heating them with quinoline is the formation of a six-membered ring with conjugated double bonds, as was to be expected from the reaction outline proposed.

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Received December 30, 1949.

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THE ACTION OF ALUMINUM AMALGAMS ON 3-CHLORO-3-METHYLBUTYNE-1

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The 1,2-diene hydrocarbons are a theoretically interesting class of organic compounds because of the peculiar nature of the allene bond Not much work has been done on allene hydrocarbons, however, because of the difficulty of securing them in the pure state Ya I Ginsburg [1] worked out a new method of preparing allene hydrocarbons, involving the reduction of unsaturated chlorides (I or II) in a butyl alcohol solution by zinc dust in the presence of a Cu bronze.

$$(CH_3)_2C(Cl)-C\equiv CH \xrightarrow[ROH]{Zn,Cu} (CH_3)_2C=C=CH_2$$

[I]

$$(CH_3)_2C=C=CHCl \xrightarrow[ROH]{Zn,Cu} (CH_3)_2C=C=CH_2$$

[II]

The yield of as-dimethylallene was 65-85% of the theoretical The ready availability of chlorine derivatives of these types [2] makes the Ya. I Ginsburg method quickest and best for snythesizing allene hydrocarbons.

We decided to explore the similar process of reducing 3-chloro-3-methylbutyne-1 with aluminum amalgam.

We know that the reduction of allyl halogen derivatives with various metals yields a mixture of hydrocarbons, the composition of the mixture depending upon the metal employed [3] We were interested in learning whether pure dimethylallene would be produced by reacting the acetylenic chloride (I) with aluminum amalgam, as Ya. I. Ginsburg had done when he employed zinc dust as the reducing agent.

The acetylenic chloride (3-chloro-3-methylbutyne-1) was reduced with aluminum amalgam in a water-alcohol medium by heating it to the boiling point of the solution. The resulting low-boiling hydrocarbons were driven off as they were formed. The liquid collected in a series of tests was washed free of its alcohol with water, desiccated with $CaCl_2$, and distilled in vacuum, the following fractions being collected: 1) 28-31°, 5.1 g; 2) 31-39.5°, 11.5 g; and 3) 39.5-42°, 1.7 g.

All the fractions exhibited a positive reaction for acetylenic hydrogen and contained no halogen. A narrower fraction (32-35°) was isolated from the middle fraction and tested with maleic anhydride to determine whether it contained isoprene; no condensation product was found.

The structure of the hydrocarbons contained in Fractions 1 and 2 was determined by hydrating them to the respective ketones. Fraction 1 yielded a ketone that gave a p-nitrophenylhydrazone with a m p. of 107-109°, which is the melting point of the p-nitrophenylhydrazone of methyl isopropyl ketone Hence, the hydrocarbon was isopropylacetylene.

Constants of Fraction 1: b.p. 28-31°; n_D^{20} 1.37586.

Constants of isopropylacetylene: b.p. 28-29°; n_D^{20} 1.37396[4].

Hydration of Fraction 2, with a b.p. of 32-35°, yielded a ketone that gave a semicarbazone with a m.p of 168-170°, which is the melting point of the semicarbazone of methyl isopropenyl ketone [5]. A fusion sample mixed with the specially prepared semicarbazone of methyl isopropenyl ketone had the same melting point. These facts are evidence that Fraction 2 contained the hydrocarbon isopropenylacetylene.

Constants of Fraction 2: b.p. 32-35°; $n_D^{23.1}$ 1.40307.

Constants of isopropenylacetylene: b.p. 32-32.5°; n_D^{20} 1.4158[6].

Fraction 3, with a b.p. of 39.5-42° and a n_D^{20} 1.40765, was nearly pure as-dimethyl-allene, the constants of which are given in the literature as follows:

B.p. 39-41°; n_D^{20} 1.40904 (Slobodin) [7].

B.p. 39.5-40.5°; n_C^{13} 1.4216 (Ya. I.Ginsburg) [1].

Thus, reacting 3-chloro-3-methylbutyne-1 with aluminum amalgam in a water-alcohol solution at the latter's boiling point yields a mixture of the following hydrocarbons: about 30% isopropylacetylene; about 60% isopropenylacetylene; and about 10% as-dimethylallene.

EXPERIMENTAL

Reduction of 3-Chloro-3-methylbutyne-1

Reduction was effected in a flask fitted with a three-piece adapter, a reflux condenser, a dropping funnel, and a stirrer. The chloride solution was added a drop at a time, with continuous stirring, to the boiling ethyl alcohol with the aluminum amalgam immersed in it. 3 mols of Al amalgam, 270 ml of alcohol, and 60 ml of water were used per mol of the acetylenic chloride The resulting hydrocarbon was driven off through the reflux condenser, the alcohol and the chloride condensing and returning to the reaction flask Repeated tests yielded a quantity of liquid, which was washed with water to free it of its alcohol and then desiccared with $CaCl_2$ Fractionation yielded three principal fractions:

Fraction 1: 28-31°; n_D^{20} 1.37586;

Fraction 2: 32-35°; $n_\alpha^{23.1}$ 1.39962; $n_D^{23.1}$ 1.40307;

Fraction 3: 39.5-42°; n_D^{20} 1.40765.

Hydration of the hydrocarbon with a b.p. of 28-31°. 2.1 g of the hydrocarbon was added to a saturated solution of mercuric chloride, a white precipitate of the mercury derivative settling out. After an hour had passed, hydrochloric acid was added to the turbid solution, which was then distilled. The distillate was collected in a solution of p-nitrophenylhydrazine acetate. The resultant p-nitrophenylhydrazone had a m.p. of 107-109°.

Hydration of the hydrocarbon with a b.p. of 32-35°. This hydration was performed in the same way. The resultant distillate was collected in a solution of semicarbazide acetate, from which the semicarbazone soon precipitated out. The product had a m.p. of 168-170° after three recrystallizations from absolute alcohol. A fusion sample exhibited no depression when mixed with the specially prepared semicarbazone of methyl isopropenyl ketone (m p.170°).

SUMMARY

The reduction of 3-chloro-3-methylbutyne-1 with aluminum amalgam in boiling aqueous ethyl alcohol yields a mixture of the following hydrocarbons: isopropylacetylene, isopropenylacetylene, and as-dimethylallene.

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Received December 29, 1949

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THE ELECTROLYTIC HYDROGENATION OF DIACETYLENIC GLYCOLS

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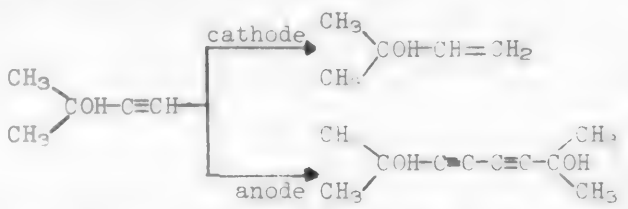
In the electrolytic hydrogenation of dimethylacetylcarbinol without separating the electrodes we succeeded in showing [1] that under certain conditions (the presence of a copper cathode or of copper salts in the electrolyte) the reaction may take place in such a way as to produce dimethylvinylcarbinol at the cathode and dimethyl-2,7-octadiyne-3,5-diol-2,7 at the anode:



Further exploration of progressive electrolytic hydrogenation and an extension of the initial diagram of ours required that we investigate the behavior of a diacetylenic glycol when acted upon by electrolytically nascent hydrogen. On the one hand, it might be supposed that a certain equilibrium would exist between an acetylenic alcohol and a diacetylenic glycol in the presence of copper salts and in an alkaline electrolyte, the diacetylenic glycol formed breaking down again under the action of the hydrogen to form two molecules of the acetylenic alcohol and the latter then being hydrated to an ethylenic alcohol. An example of such a rupture of a single bond is found in Bayer's reduction of diacetylenedicarboxylic acid with sodium amalgam [2]. In addition to hydromuconic acid, Bayer also secured a considerable quantity (2/3 of the total) of propionic acid. The diacetylenedicarboxylic acid was first cleaved at the single bond, yielding two molecules of propiolic acid, which was then reduced to propionic acid. Bayer secured even more interesting results when he reduced the ethyl ester of diacetylenedicarboxylic acid with zinc dust in hydrochloric acid, propargyl ether being produced. The hydrogen first cleaved the ethyl ester of diacetylenedicarboxylic acid, yielding two molecules of the propiolate, after which the carbonyl group of the propiolate was reduced, forming ethyl propiolyl ether, the triple bond remaining untouched:

$$C_2H_5OCO-C\equiv C-C\equiv C-COOC_2H_5 \rightarrow 2HC\equiv COOC_2H_5 \rightarrow 2HC\equiv C-CH_2OC_2H_5$$

A check showed that the reduction of ethyl propargylate under these conditions likewise yielded ethyl propargyl ether. When Bayer performed this hydrogenation under different conditions, all he got from the diacetylenedicarboxylic acid was adipic acid.

In the literature we searched through we found no references to the electrolytic hydrogenation of diacetylenic glycols in general, or of those with conjugated triple bonds in particular. The first representative of this series of compounds, diacetylene, was first hydrogenated catalytically (with Ni, Pt, Pd, Cu, and other metals) to butadiene in 1931 [3]. According to another patent [4], diacetylene was reduced to butadiene and vinylacetylene with salts of divalent chromium, the divalent chromium being produced by electrolytically reducing salts of trivalent chromium under appropriate conditions. The treated chromium salt was reduced electrolytically and re-used for hydrogenation. We do not know why the authors made no attempt to combine the two reactions and hydrogenate diacetylene electrolytically in the presence of chromium salts. Subsequent research in this field also showed that the hydrogenation of diacetylenic compounds is for the most part a complicated matter, depending to a large extent upon the hydrogenation conditions. Research on the reduction of diphenyldiacetylene supports the argument outlined above. Reducing diphenyldiacetylene in an alcoholic solution with metallic sodium, Hollemann [5] apparently secured phenylacetylene. Here, as in Bayer's experiment, the

reducing agent cleaved the diphenylacetylene at the single bond, yielding phenylacetylene.

Straus [6] reduced an alcoholic solution of diphenyldiacetylene with copper-plated zinc dust. With light excluded, four atoms of hydrogen were added to the diphenyldiacetylene, yielding cis-cis-diphenylbutadiene. When exposed to sunlight, this labile isomer was converted into the stable trans-trans-diphenylbutadiene Straus also secured a liquid hydrocarbon with the empirical formula $C_{16}H_{12}$, which he thought was cis-diphenylbutenyne Cis-diphenylbutenyne turned into trans-diphenylbutenyne when exposed to sunlight Reducing diphenyldiacetylene in alcoholic solution with sodium amalgam yielded diphenylbutene-2.

Grignard and Tcheoufaki [7] explored the addition of hydrogen to diphenyldiacetylene in the presence of platinum oxide. Hydrogenation was effected in an alcoholic solution with light excluded. It yielded a small quantity of the original product, cis-cis-diphenylbutadiene, dibenzylacetylene, and a liquid product, to which the authors assigned the structure of diphenylbutatriene on the basis of their ozonation tests. Thus, platinum oxide causes hydrogen to be added in two ways: on the one hand, at the 1,2 and 3,4 positions, contrary to Thiele's theory, yielding diphenylbutadiene, and on the other, in aggrement with Thiele, at the 1,4 position, yielding diphenylbutatriene, to begin with, and then dibenzylacetylene. Why the further addition of hydrogen should come to a stop is unclear. A catalyst like platinum oxide might have been expected to yield saturated hydrogenation products. This is borne out by the researches of Lespieau [8], who showed that alcoholic solutions of acetylenic and diacetylenic glycols are reduced by platinum black to saturated compounds, a small quantity of saturated monoatomic alcohols and hydrocarbons always being formed, it seems. Kuhn and Wallenfels [9] secured several diethylenic glycols from the respective diacetylenic glycols by hydrogenating them catalytically with palladium on barium sulfate. The authors stopped hydrogenation after two atoms of hydrogen had been added, however, since continuing the supply of hydrogen in the presence of that catalyst resulted in the formation of saturated glycols.

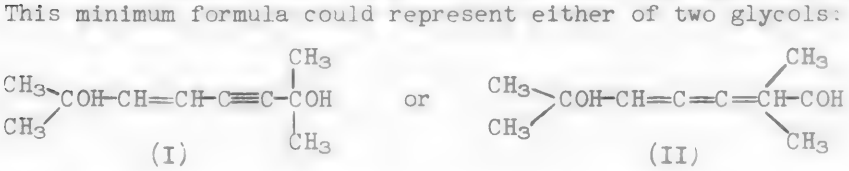
The foregoing brief review of the data in the literature indicates that the hydrogenation of diacetylene derivatives cannot be described by means of a single set of reactions. Though hydrogen is added at the 1,4 position in some cases, in others it is added at the 1,2 and 3,4 positions, while in still others it is added simultaneously in all possible ways.

In the present research we desired to find out whether it is possible to effect the step-by-step hydrogenation of diacetylenic glycols under the conditions elaborated by us for acetylenic alcohols and glycols [10]. With this as our objective, we ran a series of tests on the elctrolytic hydrogenation of dimethyl--2,7-octadiyne -3,5-diol-2,7. At the start hydrogenation was performed at a copper cathode in an aqueous solution of sodium hydroxide. The glycol was almost insoluble in this electrolyte, however. We therefore used as our electrolyte dilute ethyl alcohol (2:1 by volume) Using porous diaphragms increased the yield and the purity of the products of the electrolytic hydrogenation of dimethyloctadiynediol. The electrolytic hydrogenation of dimethyl-2,7-octadiyne -3,5-diol-2,7 yielded an oily liquid that had a boiling point of 70-72° (2 mm) after repeated distillation, plus crystals. In addition, there remained in the electrolyte a friable white mass that was not crystalline in structure and did not dissolve in the usual solvents (water, alcohols, ether, benzene). The 70-72° (2 mm) had a fragrant odor; analysis proved it to be a diethylenic alcohol-dimethyl-2,7--octadien-2,4-ol-7 - a homolog of linalool. A more detailed analysis of this

fraction has been published in one of our previous papers [1], so that we shall omit it here. We were able to divide the crystals into two fractions after repeated recrystallization from (40-60°) petroleum ether and benzene. The first fraction had a m.p. of 73-76°, the m.p. of the second being 82-84°.

The crystals with a m.p. of 82-84° were freely soluble in cold water, whereas the original dimethyloctadiynediol was only slightly soluble in hot water. Its empirical formula was $C_{10}H_{18}O_2$. In the determination of the degree of unsaturation of the glycol by titrating it with an aqueous bromide-bromate solution, 95% of bromine was added, based on two double bonds or one triple one. In the catalytic hydrogenation with platinum black 105% of hydrogen was added (again based on two double bonds or one triple one). The resultant saturated glycol had melting points of 59-60° (from water) and 90-91° (from benzene), which agrees with the figures given in the literature for dimethyl-2,7-octanediol-2,7 [11]. The structure of the crystals with a m.p. of 82-84° was determined by oxidizing them with an aqueous solution of permanganate. Oxidation yielded acetone, oxalic acid, and, apparently, a mixture of β-hydroxyisovaleric and α-hydroxyisobutyric acids. The resultant oxidation products indicated that the crystals with a m.p. of 82-84° were not homogeneous, but constituted a mixture of two glycols: the diethylenic dimethyl-2,7-octadiene-3,5-diol-2,7 and the acetylenic dimethyl-2,7-octyne-4-diol-2,7.

The crystals with a m.p. of 73-76° had the empirical formula of $C_{10}H_{16}O_2$. This minimum formula could represent either of two glycols: (I) and (II)



(I) or (II)

This fraction was not analyzed any further.

In our initial experiments on the electrolytic hydrogenation of dimethyloctadiynediol we noticed, during our processing of the hydrogenation products, that the electrolyte contained insoluble crystals. These crystals were washed with a large quantity of water and placed in a vacuum desiccator with calcium chloride to dry. After some time (1-2 hours) had elapsed, we found that the substance had changed into an amorphous state without losing its external crystalline appearance and had become rubbery. Before desiccation the crystals had been freely soluble in benzene, but the amorphous substance merely swelled up in it. When the substance was kept in the desiccator for a longer time, it became tacky, like a gum. The presence of peroxide compounds in it was proved qualitatively. The best determination of its empirical formula we could make in some cases was $C_{10}H_{16}O_4$.

The foregoing indicates that the electrolytic hydrogenation of diacetylenic glycols at a copper cathode in an alkaline electrolyte is not as simple as we found it to be in the case of acetylenic alcohols and alcohols. Apparently, in this instance the hydrogen is added in all possible ways. Adding hydrogen at the 1,4 position yields dimethyloctenediol, in addition to other products, this diol loses one molecule of water and is converted into dimethyl-2,7-octadien-2,4-ol-7, which we had identified previously. This splitting out of one molecule of water is quite possible under the conditions of hydrogenation. The glycol with a m.p. of 82-84° gave up water after standing for only one day in a vacuum desiccator above sulfuric acid, turning into a tacky polymer mass.

We conducted electrolytic hydrogenation in a hermetically sealed electrolyzer, measuring all the hydrogen added, as well as in an open hydrolyzer (without calculating the added hydrogen). 13.25 ampere-hours of electricity resulted in the

addition of 4180 ml of hydrogen, equivalent to about three molecules of hydrogen for the quantity of dimethyloctadiynediol we had used (10 g). The variety of products we secured in this electrolytic hydrogenation made it impossible, however, to draw any inference concerning the composition of the end products of the reaction from the amount of hydrogen added to the diacetylenic glycol

EXPERIMENTAL

The dimethyloctadiynediol was hydrogenated electrolytically in a glass electrolyzer. A perforated sheet of copper, coated with a layer of cupric oxide by heating it over a gas flame, served as the cathode. The cathode had a surface of 1.8 sq dm, while the cathode C.D. was 0.8 amp/sq dm. The catholyte contained 10 g of dimethyloctadiynediol, 0.5 g of sodium hydroxide, and 150 ml of 96% ethyl alcohol, the volume of the catholyte being brought up to 220 ml by the addition of water. The anode was a nickel helix placed in a porous cylinder 155 mm high, 37 mm I.D., and with a wall 4 mm thick. The anolyte consisted of 100 ml of a saturated aqueous solution of sodium hydroxide. The results of hydrogenation are listed in Table 1.

TABLE 1

Ampere-hours	Yield of liquid products	Yield of crystalline products			Hydrogen added	Remarks
		Original glycol	Glycol with a m.p. of 82-84°	Glycol with a m.p. of 73-76°		
13.25	33-45° (22 mm) 15%	34%	30%	15%	4180 ml	The liquid product did not have a pleasant odor
20	70-72° (2 mm) 39%	None	38%	8%	disregarded	

In our first test the electrolyzer was hermetically sealed, and we measured the amount of hydrogen added. In the second test the current was increased 50%, and the hydrogen was not measured. In the hermetically sealed electrolyzer we got no fraction with a b.p. of 70-72° (2 mm), nor any "polymer." In the first test we secured 1.8 g of liquid and 8 g of crystals, which had the following melting points after repeated crystallization from benzene. Fraction I: 130-131°, 3.4 g; Fraction II: 82-84°, 3.0 g; and Fraction III: 73-76°, 1.5 g.

The second test yielded the following fractions: Fraction I. 65-70° (3 mm), 0.2 g; Fraction II: 70-72° (2 mm), 3.9 g; and Fraction III: 5.0 g of a crystalline residue in the flask. Repeated recrystallization of the crystalline residue from petroleum ether (40-60°) and from benzene yielded crystals that had the following melting points. Fraction I: 73-76°, 0.8 g; and Fraction II: 82-84°, 3.8 g. The test was run four times to collect enough of the products.

Analysis of the Crystals With a M.P. of 82-84°

0.1088 g substance: 0.2805 g CO_2; 0.1038 g H_2O; 0.0946 g substance: 0.2433 g CO_2; 0.0909 g H_2O. Found %: C 70.31, 70.20; H 10.68, 10.75. $C_{10}H_{18}O_2$. Calculated %: C 70.55; H 10.66. 0.0743 g substance: 7.7 ml bromide-bromate; 0.0700 g substance: 7.2 ml bromide-bromate (titer = 0.01574 g/ml). % Br added: 61.99, 61.83. $C_{10}H_{18}O_2Br_4$. Calculated %: Br 65.25.

Catalytic Hydrogenation

0.3060 g substance: 0.25 g Pt, 80 ml absolute ether. 84 5 ml hydrogen added (91 ml at 20° and 764 mm). $C_{10}H_{22}O_2$. Calculated: 80.6 ml hydrogen.

Driving off the ether yielded 0.4 g of crystals with a m.p. of 90-91° (from benzene), corresponding to dimethyl-2,7-octanediol-2,7.

Oxidation with an aqueous solution of permanganate. We took 3 g of the crystals with a m.p. of 82-84° and 15 g of $KMnO_4$ dissolved in 500 ml of water (part of the permanganate being in powder form) for oxidation. The solution was decolorized very quickly when the permanganate was poured in. The resultant neutral products included acetone, identified as its p-nitrophenylhydrazone, which had a m.p. of 148° and exhibited no depression when mixed with the known product. The solution left after the neutral products had been driven off was acidulated with the calculated quantity of sulfuric acid. Ether was used to extract 1 5 g of a syrupy liquid from the acid solution in a percolator. When the syrup was allowed to stand in a vacuum desiccator over sulfuric acid, crystals settled out, which had a m.p. of 187-188.5° after twofold sublimation and exhibited no depression when mixed with oxalic acid. The residue, which did not crystallize after standing for a long time in a vacuum desiccator, was converted into a silver salt, 0.5 g of the silver salt being obtained.

0.1946 g substance: 0.0948 g Ag; 0.2140 g substance: 0.1044 Ag. Found %: Ag 48.72, 48.80. $C_4H_7O_3Ag$. Calculated %: Ag 51.16. $C_5H_9O_3Ag$. Calculated %: Ag 47.96.

Thus the syrup apparently consisted of a mixture of α-hydroxybutyric and β-hydroxyvaleric acids.

Analysis of the Fraction With a M.P. of 73-76°

0.1064 g substance: 0.2789 g CO_2; 0.0943 g H_2O; 0.1244 g substance: 0.3250 g CO_2; 0.1078 g H_2O. Found %: C 71.47, 71.25; H 9.92, 9.70. $C_{10}H_{18}O_2$. Calculated %: C 71.37; H 9.59.

Analysis of the "polymer." After electrolysis was complete, the electrolyte was extracted with ether. The portion that was insoluble in ether was washed with water and desiccated in a vacuum desiccator with $CaCl_2$. The solid white product gradually turned during desiccation into a tacky gummy mass which exhibited a positive reaction for peroxides (with KI). Combustion yielded extremely varying results: the % C fluctuated from 68 to 61%, while the % H fluctuated from 9 to 8%. The product did not dissolve in any of the common solvents.

SUMMARY

1 In the electrolytic hydrogenation of diacetylenic glycols with copper in an alkaline electrolyte the addition of hydrogen takes place in all possible ways at once.

2. The electrolytic hydrogenation of dimethyl-2,7-octadiyne-3,5-diol-2,7 yields a diethylenic alcohol, dimethyl-2,7-octadien-2,4-ol-7, plus some unsaturated glycols of unknown structure.

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Received February 24, 1950.

SYNTHESIS AND PROPERTIES OF METHYL VINYL ETHER

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Methyl vinyl ether is the first member of the homologous series of alkyl vinyl ethers, though for a long time it remained a compound about which little was known. The present research had as its objective the filling of this void. A study of the conditions required for the synthesis of methyl vinyl ether, which is a gaseous compound at room temperature, is interesting on its own account. From the practical standpoint, methyl vinyl ether is of interest as the raw material for the synthesis of various preparations, especially the unusual water-soluble polymers. The theoretical interest attached to this compound stems from the fact that it is the first derivative of vinyl alcohol, whose hydroxyl hydrogen is replaced by a methyl group. We were therefore greatly interested in the stability of this compound, in view of the instability of vinyl alcohol. The ability of the ether as well as of its hydrohalogenation products to exhibit tautomerism is also of considerable interest.

The patent literature indicates that methyl vinyl ether was produced for the first time in 1928 from a complicated mixture, using a mixed catalyst [1]. The patent does not even give its constants. In 1930 it was prepared by decomposing dimethyl acetal catalytically [2]. It was also synthesized by reacting vinyl halides or halogenated hydrocarbons and methyl alcohol with an alkali in a solvent medium [3]. In 1932 Chalmers [4] synthesized it (b.p. 12-14°) from ethylene oxide via the methyl ester of ethylene glycol bromohydrin. Although the cited boiling point of methyl vinyl ether is far from the true one, the author's ultimate analysis proved to be close to that of the actual ether. At this time numerous patents were issued to I.G Farbenindustrie in many countries, covering the synthesis of vinyl ethers by the addition of alcohols to acetylene. These methods were based upon the A.E.Favorsky reaction [5], dealing with the addition of ethyl alcohol to allylene in the presence of potassium hydroxide. As in the Chalmers synthesis, the authors of the patents cited [6] confine themselves to mentioning the fact that methyl vinyl ether had been synthesized, giving its boiling point as 9°. Numerous patents stress the necessity of diluting the acetylene with nitrogen in every case, including the synthesis of methyl vinyl ether. In 1939 Favorsky and Shostakovsky [7] developed a new method for preparing vinyl ethers, starting with undiluted acetylene and various alcohols and using potassium hydroxide as the catalyst. The use of undiluted acetylene was based upon the fact that the reaction first occurs in a solution of alcohols, and in the respective ether toward the end of the synthesis. As for methyl vinyl ether, Favorsky and Shostakovsky did synthesize it, but did not secure it in a sufficiently individual state, its boiling point, in particular, turning out to be 9-10°. These authors synthesized this ether as 10% solution in methanol. Moreover, the synthesized methyl vinyl ether was not refined as it should have been to determine its physicochemical constants. It should be said that these constants are completely absent in the other papers mentioned, a boiling point of 8.0 - 8.3° being cited for methyl vinyl ether only in a paper on Raman spectra [8]. According to these authors, the ether was distilled with metallic sodium into a Davis column. Furthermore, it is stated in a paper on the polymerization of methyl vinyl ether [9] that the authors employed an ether with the following constants: b.p. 12°, d_0^0 0.9938.

Thus none of the references in the literature dealing with the synthesis of methyl vinyl ether or with its conversions gives its physico-chemical constants, the various authors giving widely different figures for its boiling point, in particular.

The story of the determination of the boiling point of ethyl methyl ether [10], for which the following values were cited: 10.8°, 6.4°/724 mm, 11-12°, has been repeated to the last detail in the case of methyl vinyl ether. The best of the foregoing figures is considered to be 6.4°/724 mm. In our opinion, even this latter temperature is hardly the true boiling point.

When we made a comparison long ago of the boiling points of vinyl ethers with those of the corresponding saturated analogs, we noted a certain regularity of pattern. The vinyl ethers of monoatomic aliphatic alcohols have boiling points that are 1-4° higher than the respective saturated ethyl ethers. There is a somewhat greater difference between the boiling points of vinyl and ethyl glycol ethers. The vinyl ethers of glycerol, on the other hand, have boiling points that are 2-5° below those of their saturated analogs. The analogous phenol ethers behave like the glycerine ethers insofar as their boiling points are concerned, but the differences are nearly 15° in this case. In the case of the aliphatic-aromatic alcohols, the differences between the boiling points of their vinyl and ethyl ethers are closer to those prevailing in the aliphatic series (see table).

Methyl vinyl ether was synthesized by the Favorsky and Shostakovsky method [7]. The methanol was vinylated very easily, though the pressure within the autoclave rose to a very high value because of the low boiling point of methyl vinyl ether. Of the methods of purifying methyl vinyl ether, the most satisfactory proved to be the general methods given for the refining of alkyl vinyl ethers [12]. Provided vinylation is complete, a pure methyl vinyl ether is secured after two fractionations. The ether may be successfully freed of any alcohol by washing it with ice water or, better still with a strong solution of alkali. The water is eliminated by desiccating the ether with calcined potash. Any traces of moisture or alcohol are removed excellently by treating the ether with metallic sodium. The methyl vinyl ether distils with the latter without any decomposition.

In view of the discrepancies existing in the literature concerning the constants of methyl vinyl ether, we paid special attention to the purity of the ether when we determined its constants. We fractionated it and determined its molecular weight and refraction when the air temperature ranged from +1 to - 12°. The constants thus determined proved to be nearly identical with the figures given by the American authors of the survey article [11], which appeared after our investigations had been completed. This article reproduces solubility curves of methyl vinyl ether in water and of water in the ether, plus curves giving the specific gravity as a function of temperature, and the boiling point as a function of pressure, in addition to other data.

Methyl vinyl ether has the general properties that are typical of all alkyl vinyl ethers. Its structure has been established by means of hydrolysis and bromination reactions.

Methyl vinyl ether may be successfully employed for the manufacture of acetaldehyde and dimethyl acetal, for the manufacture of its polymers or copolymers, and as a raw material for organic synthesis.

EXPERIMENTAL

Synthesis of Methyl Vinyl Ether

$$CH_3OH + HC{\equiv}CH \xrightarrow{(KOH)} CH_2{=}CH{-}O{-}CH_3$$

TABLE

Comparative Boiling Points of the Vinyl and Ethyl Ethers of Various Alcohols

No	Boiling point of the ethers			
	Formula	Boiling point	Formula	Boiling point
1	$CH_2{=}CH{-}OCH_3$	5.5°	$C_2H_5OCH_3$	6.4°
2	$CH_2{=}CH{-}OC_2H_5$	36	$C_2H_5OC_2H_5$	35
3	$CH_2{=}CH{-}OC_3H_7$	65	$C_2H_5OC_3H_7$	63.6
4	$CH_2{=}CH{-}OC_3H_7$	55.1-55.7	$C_2H_5OC_3H_7$	54
5	$CH_2{=}CH{-}OC_4H_9$	93.8	$C_2H_5OC_4H_9$	91.4
6	$CH_2{=}CH{-}OC_4H_9$	83	$C_2H_5OC_4H_9$	79
7	$CH_2{=}CH{-}OC_5H_{11}$	112.5-112.8	$C_2H_5OC_5H_{11}$	112
8	1) $CH_2{=}CH{-}OCH_2$ CH_2OH	140	$C_2H_5OCH_2$ CH_2OH	135
	2) $CH_2{=}CH{-}OCH_2$ $CH_2{=}CH{-}OCH_2$	126.8	$C_2H_5OCH_2$ $C_2H_5OCH_2$	123.5
9	1) $CH_2{=}CHOCH_2$ $CHOH$ CH_2OH	229-230	$C_2H_5OCH_2$ CH_2OH CH_2OH	231-232
	2) $CH_2{=}CH{-}OCH_2$ $HO{-}CH$ $CH_2{=}CH{-}OCH_2$	184-185	$C_2H_5OCH_2$ $HO{-}CH$ $C_2H_5OCH_2$	190
	3) $CH_2{=}CH{-}OCH_2$ $CH_2{=}CH{-}OCH$ $CH_2{=}CH{-}OCH_2$	164	$C_2H_5OCH_2$ C_2H_5OCH $C_2H_5OCH_2$	166
10	$CH_2{=}CH{-}OC_6H_5$	155-156	$C_2H_5OC_6H_5$	170.3
11	$CH_2{=}CHOCH_2C_6H_5$	183-184	$C_2H_5OCH_2C_6H_5$	185

A solution of 40 g of potassium hydroxide in 400 g of purified anhydrous methanol (99 2%, b.p. 64-67° d_4^{20} 0.7941, n_D^{20} 1.3304), was charged into a thick-walled, rotating (1 rps) Bergius autoclave, equipped with a Hofer valve, an acetylene manometer, a jacket for a thermometer, and an electric-heating jacket. The acetylene was fed into the autoclave from a gas cylinder. The latter was also, sometimes used to drive the remaining air out of the autoclave. After the system had been tested for gas-tightness, the motor and the heating coil were connected. When the temperature of the reaction mass had reached 140°, the heating current was turned off, and the mass was allowed to heat up to 150°, after which the upper section of the heating jacket was quickly opened. This cooled the rotating autoclave to room temperature, its internal pressure dropping to 0 - 2 atm. Then a new batch of acetylene was fed into the autoclave and the reaction producedure was repeated. Acetylene was added in this manner as long as it entered into the reaction sufficiently, after which the absorption of acetylene stopped. This latter factor is the best indication of the end of vinylation.

In this experiment the maximum temperature of the reaction mass varied from 147 to 153°. Acetylene was supplied from the cylinder 21 times at a pressure of 9-8 atm. The maximum pressure within the autoclave, observed at 150°, rose from 20 atm after the initial charge of acetylene to 60 atm after the last one, rising in proportion to the accumulation of methyl vinyl ether within the autoclave. It is not advisable to allow the pressure to go any higher in this experimental procedure. The residual pressure within the autoclave rose during the reaction from zero to 2 atm as the ether accumulated, being 7 atm before the autoclave was emptied. The quantity of acetylene that reacted, calculated from the manometer readings at 20°, totaled 328 liters (152 liter/atm), or 355 g, instead of the 295 liters (20°) or 319.3 g that our calculations had indicated was required. We attribute this apparent excess consumption to inaccuracies in the manometer readings, its large scale graduations (2 atm), and the large number of readings taken. It may be added that the acetylene employed was of commercial grade.

The synthesized ether was discharged via a valve connected by a nipple and a rubber hose to a system of receivers arranged in succession in a freezing mixture (-15° to -10°). The receivers consisted of a 1 2-liter three-necked Woulfe bottle, fitted with an efficient vertical coil condenser and two similar 200-ml and 100-ml traps. The latter trap was connected to a Tishchenko bottle containing methanol, immersed in the freezing mixture, which was used to check the rate at which the unreacted acetylene was exhausted and the rate at which the ether was transferred to the receiver.

The first thing to be discharged from the autoclave after it had cooled down to room temperature was the acetylene. When the pressure fell to 2 atm, the ether began to distil off. Provided the acetylene is let out gradually and the ether is thus distilled equally slowly, the latter condenses with almost no loss in the Woulfe bottle, and partially in the first trap. In this test nearly all the ether distilled at about 20°. Toward the end of distillation the autoclave was reheated to 40° to assure complete evacuation of the synthesized ether. The chilled distillate was a wholly transparent, colorless, highly mobile ethereal liquid with the obvious odor of acetylene. The yield totaled 690 g (96.4% of the theoretical). The walls of the autoclave were found to be dry when it was opened. The absolutely dry catalyst lay at the bottom of the autoclave as gray, roundish pieces.

A parallel test (No.2), using the same operational procedure and with the same charges of the constituents specified above, but without first clearing out the air from the autoclave, yielded 680 g (95% of the theoretical) of the ether. During this test acetylene was charged 18 times from the cylinder at a pressure of 12-8 atm. The maximum temperature of the reaction mass varied from 150 to 153°, superheating to 160° occurring in two instances. The initial batch of acetylene produced a pressure of 20 atm at 150°, the pressure produced by the last batch being 55 atm. After the last batch of acetylene had been added the residual pressure totaled 11 atm. The acetylene consumption, read off from the manometer, totaled 348 liters (161 liters/atm) or 376 g. The apparent excess consumption of acetylene totaled 18%.

Purifying methyl vinyl ether. Various methodswere tried out. The alcohol was driven out of the ether by simple distillation, washing the distillate with an alkali solution and then treating it with metallic sodium. Calcined potash and metallic sodium were used as drying agents. Distillation was done over a water bath (7-20°) from a Favorsky flask (fitted with a herringbone dephlegmator) with a stem immersed thermometer. The condenser employed was a high-power vertical coil, chilled with a snow-and-salt mixture (-10 to -15°). The condenser was connected via an adapter to the receiver flask, immersed in snow. A trap fitted with a coil condenser and protected against outside moisture by a tube filled

with calcium chloride, and immersed in the freezing mixture, was connected to an extension of the adapter. In view of the fact that the vapor of the ether attacks rubber, the distillation apparatus was equipped with cork stoppers.

The samples of the ether we obtained were tested qualitatively for the presence of any acetylene or aldehydes. The refraction and the specific gravity of samples of the pure ether were determined. The presence of acetylene was determined by means of an Ilosvay reagent, acetaldehyde being detected by means of an aqueous solution of Schiff's reagent, and the latter reagent being acidulated to detect formaldehyde.

The original ether was stored in the cold in glass bottles with cork stoppers and in sealed ampoules only 2/3 filled at room temperature. The research was done in a wintry room, the air temperature of which ranged from + 1 to -12°.

1) Purification by simple distillation We cite below the fractionation data of methyl vinyl ether.

Fractionation 1. Test 1 690 g used for fractionation Yield (at 760 mm): Fraction 1 2-5.9°, 665 g; residue 5 g; losses 20 g. Test 2. 430 g used for fractionation Yield (at 760 mm): Fraction 1: 0-6.5°, 400 g; residue 12 g; losses 18 g.

Both of these fractions were transparent colorless liquids with the characteristic odor of a vinyl ether, which exhibited a positive reaction for acetylene. The residues gave an unmistakable positive reaction for acetylene.

Fractionation 2. The first fractions of both tests above were refractionated, each of them being dried with calcined potash before fractionation. Test 1 650 g fractionated. Yield (at 745 mm): Fraction 1: 3.0 - 5.0 g, 10 g; Fraction 2: 5.0 - 5.2°, 616 g (the bulk at 5°); residue 6 g; losses 18 g. Test 2. 390 g fractionated. Yield (at 753 mm): Fraction 1: 2.0 - 5.0°, 5 g; Fraction 2: 5.0 - - 6.0°, 361 g (the bulk at 5.3°); residue 5 g; losses 19 g.

The second fractions of both tests had the same refractive index (n_D^o 1.3730) and exhibited an extremely faint reaction for acetylene. The first fractions exhibited a negative reaction, while the colorless residues had positive reactions for acetylene.

Fractionation 3 71 g of the ether, represented by Fraction 2 of Test 1 (b.p. 5.0 - 5.2° at 745 mm), was distilled at 743 mm without any preliminary treatment. Yield: Fraction 1: 4.2 - 5.0°, 2 g; Fraction 2: 5.0°, 60 g; residue 5 g; losses 4 g.

Neither acetylene nor aldehydes was found in either of these two fractions. The refractive index of Fraction 2 was the same as that of the original sample, (n_D^o 1.3730). The colorless residue exhibited a barely perceptible reaction for acetylene.

2) Purifying methyl vinyl ether by washing with a 10% solution of potassium hydroxide. The solubility of the original ether in slightly alkalinized water was no higher than 2% at + 1°. When a 10% alkali solution is used, the solubility may be tested at lower temperatures, owing to the depression of the freezing point of this solution, thus enabling us to do the purifying at temperatures below 0° (down to -9°), which allowed for the low boiling point of the original ether. The pure methyl vinyl ether was secured by a preliminary washing, followed by desiccation and fractionation.

250 g of the ether from the autoclave (Test 2) was washed three times in

a separatory funnel with a 10% alkali solution, twice as much alkali solution being used as the ether. The transparent, colorless ether recovered was dried twice in succession with potash and then fractionated. This yielded the following fractions (at 738 mm): Fraction 1: 1.0 - 4.8°, 8 g; Fraction 2: 4.8° 142 g; Fraction 3: 4.8 - 5.0°, 32 g; Fraction 4: 5.0 - 5.7°, 15 g; residue 5 g losses 48 g.

These fractions were colorless, transparent liquids, with the specific odor of a vinyl ether. The residue was a hardly perceptible yellow. A qualitative test for acetylene indicated that no acetylene was present in Fractions 1 and 2, while the quantity present in Fractions 3 and 4 and in the residue was negligible. No aldehydes were detected anywhere. The bulk of the ether distilled as Fraction 2 and had a refractive index of n_D^o 1.3730.

3) Purifying methyl vinyl ether with metallic sodium. a) Behavior of metallic sodium with methyl vinyl ether after triple fractionation. For this we used the second fraction collected in the third fractionation. The ether was allowed to stand overnight in the distilling flask with the metallic sodium that was later used for distillation. The following fractions were secured at 727 mm: Fraction 1: 4.5°, 53 g; Fraction 2: 4.5 - 4.7°, 4 g, residue 1 g, losses 2 g. The metallic sodium reacted with this sample very faintly, and then only at the start. Toward the end of distillation the sodium remained almost unaffected. The refractive index of the ether thus purified proved to be the same as that of the original ether (n_D^o 1.3730). No acetylene nor aldehydes was found in the fractions collected or in the residue.

b) Behavior of metallic sodium with methyl vinyl ether that had been previously refined by washing with an alkaline solution and by fractionation. 130 g of this ether (Fraction 2: b.p. 4.8° at 738 mm; n_D^o 1.3730) was allowed to stand in the distilling flask for 4 hours with metallic sodium and was then distilled at 744 mm. The fractionation results were as follows: Fraction 1: 5.0°, 108 g; Fraction 2: 5.0 - 5.2°, 10 g; residue 5 g; losses 7 g. The sodium hardly reacted at all. The fractions collected and the residue were transparent, colorless liquids. No acetylene nor aldehydes was found, the refractive index of the resulting ether (Fraction 1) was the same as that of the original sample.

This refining procedure yielded a methyl vinyl ether with the following constants:

B.p. 4.5° at 727 mm, 4.8° at 738 mm, 5.0° at 744 mm, about 5.5° at 760 mm (corrected); freezing point: -124° ± 2; n_D^o 1.3730; d_4^o 0.7725 ± 0.0003, MR_D 17.120; Calc. 17.230.

Determination of molecular weight (V.Meyer method): 0.0405 g substance: 17.10 ml (20°, 755.3 mm); 0.0888 g substance. 36.75 ml (20.8°, 753.8 mm) Found: M 58.66, 60.01. C_3H_6O. Calculated: M 58.05.

Properties of Methyl vinyl ether. The ether is miscible in all proportions with all common organic solvents. It is sparingly soluble in water (about 2% at 0°) and is insoluble in polyatomic alcohols. It reacts vigorously with bromine, liberating large amounts of heat. A drop of sulfuric acid causes an extremely violent exothermic reaction, hydrochloric reacting less vigorously with the ether. It is readily hydrolyzed by weak aqueous solutions of mineral acids, yielding acetaldehyde and methanol. It is converted into a water-soluble polymer in the presence of stannic chloride. It does not react with metallic sodium, caustic alkalies, or the latter's carbonates.

SUMMARY

1. A study has been made of the conditions governing the catalytic vinylation of methanol, using acetylene undiluted with any inert gas.

2. The optimum temperature for the reaction has been found to be about 150°.

3 The pressure arising within the autoclave during the reaction depends upon the alcohol-ether ratio within the reaction mixture, as well as the initial pressure of the acetylene fed in, with the former factor predominating. The internal pressure in the autoclave sometimes rises to 55-60 atm toward the end of vinylation

4. It has been shown that the safety of working with acetylene under pressure at temperatures of some 150-160° is due to the presence of the alcohol ether solvent, even when air is present within the autoclave

5. The methods of refining methyl vinyl ether have been elaborated.

6. The constants of methyl vinyl ether have been determined for pure samples, and the figures in the literature have been corrected accordingly.

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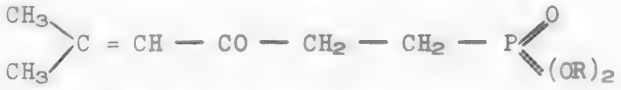
Received November 29, 1949.

THE ADDITION OF DIALKYLPHOSPHOROUS ACIDS TO UNSATURATED COMPOUNDS

II. THE ADDITION OF DIALKYLPHOSPHOROUS ACIDS TO ACRYLONITRILE AND METHYL METHACRYLATE

A. N. Pudovik and B. A. Arbuzov

In a previous report [1] we have described the addition of dialkylphosphorous acids to one of the representatives of the unsaturated ketones — β,β-dimethyl divinyl ketone. We showed that in the presence of small quantities of sodium methylate or ethylate the dialkylphosphorous acids are readily added to the unsubstituted vinyl group of the ketone, yielding ethers of the respective phosphorous acids of this general type:



Continuing our research, we were greatly interested in ascertaining the feasibility of adding dialkylphosphorous acids to compounds belonging to various other types of unsaturated compounds : unsaturated nitriles, aldehydes, esters of carboxylic acids, nitro compounds, and the like.

The present report describes the results we have secured in an investigation of the addition of dialkylphosphorous acids to two representatives of the unsaturated nitriles and the esters of unsaturated acids; acrylonitrile and methyl methacrylate. The procedure used in these reactions resembled that described in our preceding report. We found that the addition of dialkylphosphorous acids to acrylonitrile is a much more energetic reaction than their addition to β,β-dimethyl divinyl ketone. When a few drops of a highly concentrated solution of sodium methylate dissolved in methanol were added to a mixture of acrylonitrile and a dialkylphosphorous acid, the mixture grew very hot and foamed violently if no external chilling was applied. The yield of addition products usually amounted to 70-80%, going as high as 90% in some instances. As was the case with β,β-dimethyl divinyl ketone, the lower dialkylphosphorous acids, dimethylphosphorous and diethylphosphorous acids, were added most easily, with only a few drops of an alcoholic solution of sodium methylate. The higher dialkylphosphorous acids are added with much greater difficulty, much more of the alcoholate being required to complete the reaction. In every case the reaction mixture was water-cooled while the alcoholate solution was added. The constants of the addition product of diethylphosphorous acid and acrylonitrile were exactly the same as those of the phosphine ester synthesized by B. A. Arbuzov and Lugovkin by reacting β-chloropropionitrile with sodium diethylphosphite (b.p. 127-128° at 2 mm; n_D^{20} 1.4380; d_4^{20} 1.1127) [2]. Saponifying the addition product yielded phosphonopropionic acid with a m.p. of 164-165°. B. A. Arbuzov and Lugovkin give its m.p. as 166°. Comparison of the constants of our addition product of diethylphosphorous acid and acrylonitrile with those of the product synthesized by B. A. Arbuzov and Lugovkin, as well as comparison of the constants of the phosphonic acids secured in their saponification, indicates that they are very closely related, and that, therefore, the product we had synthesized was the ethyl

ester of phosphonopropionitrile[1]. The addition reaction may be represented as follows:

$$(C_2H_5O)_2POH + CH_3ONa \longrightarrow (C_2H_5O)_2PONa + CH_3OH$$

$$(C_2H_5O)_2P(=O)(Na) + {}^{+}CH_2 = {}^{-}CH - C \equiv N \longrightarrow (C_2H_5O)_2P(=O) - CH_2 - CHNa - CN$$

$$\xrightarrow{(C_2H_5O)_2POH} (C_2H_5O)_2P(=O) - CH_2 - CH_2CN + (C_2H_5O)_2PONa$$

The constants of the products of the addition of various dialkylphosphorous acids to acrylonitrile are listed in Table 1.

TABLE 1

No.	Formula	Boiling point	n_D^{20}	d_4^{20}	Per cent yield
1	$NC-CH_2-CH_2-P(=O)(OCH_3)_2$	158° at 11 mm	1.4432	1.1964	86.3
2	$NC-CH_2-CH_2-P(=O)(OC_2H_5)_2$	159-160 at 10 mm	1.4388	1.1089	83.0
3	$NC-CH_2-CH_2-P(=O)(OC_3H_7\text{-iso})_2$	160 at 13 mm	1.4345	1.0500	46.4
4	$NC-CH_2-CH_2-P(=O)(OC_4H_9\text{-iso})_2$	171 at 11 mm	1.4386	1.0359	71.0
5	$NC-CH_2-CH_2-P(=O)(OC_4H_9\text{-n.})_2$	177-178 at 11 mm	1.4395	1.0455	71.5

As we further learned, dialkylphosphorous acids can also be added to esters of unsaturated acids in the presence of sodium methylate A series of preliminary tests established that addition is much more difficult when methyl methacrylate is used than was the addition of acrylonitrile to β,β-dimethyl divinyl ketone; the reaction sets in only after a considerable quantity of a concentrated solution of sodium methylate in methanol is added to the reaction mixture, the quantity added being as much as a few milliliters in some tests. The reactions were very violent, the reaction mixture growing very hot. The reaction mixtures were then heated over a water bath for another 2-3 hours and distilled in vacuum. As in the reactions we had studied previously, the addition of dialkylphosphorous acids to methyl methacrylate may be represented as follows:

$$(RO)_2P(=O)(Na) + {}^{+}CH_2 = {}^{-}C(CH_3) - C(=O)(OCH_3) \longrightarrow (RO)_2P(=O) - CH_2 - C(CH_3)(Na) - COOCH_3$$

$$\xrightarrow{(RO)_2POH} (RO)_2P(=O) - CH_2 - CH(CH_3) - COOCH_3 + (RO)_2PONa$$

[1]) The pattern of the addition reaction is still undetermined. It may be that sodium dialkylphosphite is also added to acrylonitrile and methyl methacrylate at the 1,4 position.

The constants and yields of the reaction products are given in Table 2.

TABLE 2

No.	Formula	Boiling point	n_D^{20}	d_4^{20}	Per cent yield
1	$CH_3OOC-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-\overset{\displaystyle O}{\overset{\|}{P}}-(OCH_3)_2$	137-138° at 10 mm	1.4377	1.1761	77.7
2	$CH_3OOC-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-\overset{\displaystyle O}{\overset{\|}{P}}-(OC_2H_5)_2$	152-153° at 15 mm	1.4350	1.1212	74.5
3	$CH_3OOC-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-\overset{\displaystyle O}{\overset{\|}{P}}-(OC_3H_7\text{-iso})$	153-154° at 16 mm	1.4298	1.0612	61.0

EXPERIMENTAL

Addition of dimethylphosphorous acid to acrylonitrile. A reaction mixture consisting of 10.8 g of acrylonitrile and 22 g of dimethylphosphorous acid was chilled with cold water while a saturated alcoholic solution of sodium methylate was added from a dropping funnel. Addition of the first few drops of the methylate produced an extremely violent addition reaction, the temperature of the reaction mixture rising to 60-70°, even with cooling A few drops of sodium methylate had to be added to carry out the reaction. This produced a noticeable increase in the mixture's viscosity, the addition of more drops of the methylate no longer causing the temperature of the reaction mixture to rise any further Fractionation of the reaction mixture yielded 28.3 g of the methyl ester of β-cyanoethylphosphorous acid (Table 1, Formula 1).

0.1581 g substance: 52.9 ml NaOH (T 0 02034). Found %: P 18 8 $C_5H_{10}O_3NP$. Calculated %: P 19.0.

Saponifying the methyl ester of β-cyanoethylphosphorous acid. 8 g of the product was heated for 10 hours in a sealed tube together with 30 ml of dilute hydrochloric acid (1:1). After the tube was opened and the methyl chloride was driven off, the solution was evaporated repeatedly, distilled water being added each time. When all the hydrochloric acid had been eliminated, the solution was evaporated until it was almost dry, the resulting white solid then being dried and extracted for many hours with acetone. After most of the acetone had been driven off, the white crystals of β-carboxyethylphosphinic acid, with a m.p. of 164-165°, were recovered.

Adding diethylphosphorous acid to acrylonitrile. A saturated solution of sodium methylate in methanol was added from a dropping funnel to a chilled reaction mixture consisting of 7 g of acrylonitrile and 12 g of diethylphosphorous acid. The reaction was extremely violent, the mixture growing very warm. After 10 drops of the methylate had been added, the reaction mixture became much thicker than it was originally, though neither the temperature nor the viscosity of the reaction mixture increased when more of the methylate was added. Fractionation of the reaction mixture yielded 15.8 g of the addition product (Table 1, Formula 2).

0.1526 g substance: 43 9 ml NaOH. Found %: P 15.9. $C_7H_{14}O_3NP$. Calculated %: P 16.2

Adding di-isopropylphosphorous acid to acrylonitrile. 7 g of acrylonitrile and 21 g of di-isopropylphosphorous acid were used in the reaction, which was carried out along the lines of the previous experiments. Fractionation of the reaction mixture yielded 13.1 g of β-phosphonopropionitrile (Table 1, Formula 3).

0.1564 g substance: 40.2 ml NaOH (T 0.02034). Found %: P 14.4. $C_9H_{18}O_3NP$. Calculated %: P 14.2

Adding di-isobutylphosphorous acid to acrylonitrile. 5 g of the nitrile and 17 g of di-isobutylphosphorous acid were used, the reaction following the lines of the previous experiments. The sole difference was that much more of the sodium methylate solution had to be added to complete the reaction with di-isobutylphosphorous acid. Fractionation of the reaction mixture yielded 15.6 g of the addition product: the di-isobutyl ester of β-cyanoethylphosphinic acid (Table 1, Formula 4).

0.1500 g substance: 34.2 ml NaOH (T 0.0200). Found %: P 12.6. $C_{11}H_{22}O_3NP$. Calculated %: P 12.5.

Adding dibutylphosphorous acid to acrylonitrile. 7 g of the nitrile and 26 g of dibutylphosphorous acid were used in this reaction, a total of 2 ml of a saturated solution of sodium methylate in methanol being added to complete the reaction. Fractionation of the reaction products yielded 23.6 g of the dibutyl ester of β-cyanoethylphosphinic acid (Table 1, Formula 5).

0.1690 g substance: 36.2 ml NaOH (T 0.02034). Found %: P 11.9. $C_{11}H_{22}O_3PN$. Calculated %: P 12.5.

Adding dimethylphosphorous acid to methyl methacrylate. A saturated solution of sodium methylate in methanol was added from a dropping funnel to a reaction mixture consisting of 9 g of dimethylphosphorous acid and 9 g of methyl methacrylate. Only after 1 to 1.5 ml of the solution had been added did the reaction set in — it was very violent, the reaction mixture growing very hot. After the reaction mixture had cooled, it was fractionated in vacuum, yielding 14 g of the addition product: the methyl ester of α-methyl-β-dimethylphosphonopropionic acid (Table 2, Formula 1).

0.1603 g substance: 40.6 ml NaOH (T 0.02034). Found %: P 14.3. $C_7H_{15}O_5P$. Calculated %: P 14.7.

Adding diethylphosphorous acid to methyl methacrylate. The reaction resembled the previous one, 6.5 g of methyl methacrylate and 8 g of diethylphosphorous acid being used. Fractionation of the reaction mixture yielded 10.8 g of the methyl ester of α-methyl-β-diethylphosphonopropionic acid (Table 2, Formula 2).

0.1665 g substance: 38.0 ml NaOH (T 0.02034). Found %: P 12.74. $C_9H_{19}O_5P$. Calculated %: P 13.02.

Adding di-isopropylphosphorous acid to methyl methacrylate. 8 g of methyl methacrylate and 12 g of di-isopropylphosphorous acid were used in this reaction. The reaction was set off by adding 2 ml of a saturated solution of sodium methylate in methanol to the reaction mixture. The reaction was very violent, the reaction mixture growing very hot. Fractionation of the reaction mixture yielded 12.2 g of the methyl ester of α-methyl-β-di-isopropylphosphonopropionic acid (Table 2, Formula 3).

0.1511 g substance: 30.8 ml NaOH (T 0.02034). Found %: P 11.5. $C_{11}H_{23}O_5P$ Calculated %: P 11.6.

SUMMARY

It has been shown that in the presence of sodium alcoholates dialkylphosphorous acids are added to acrylonitrile and methyl methacrylate, yielding the respective derivatives of phosphinic acids. The structure of the resultant products has

been established and a suggested mechanism is advanced for their formation.

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Received December 23, 1949.

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THE ESTERS OF METHACRYLIC ACID

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Despite the great theoretical and practical interest attached to the esters of methacrylic acid, there are not too many papers in the literature on the synthesis or properties of the methacrylates. The references in the literature to the properties of the methacrylates [1] indicate the existence of gaps in the homologous series of the methacrylates, some of these esters not having been synthesized as yet, while the physical descriptions (boiling point, specific gravity, etc.) of others are incomplete. We were therefore interested in filling out the methacrylate series with new compounds, and in describing the physical constants and the polymerizability of as many members of the methacrylates as possible. With this as our objective we have synthesized and examined 18 esters of methacrylic acid.

Esters of methacrylic acid and the following alcohols have been synthesized and described: 1) n-hexyl, 2) sec-hexyl, 3) sec-amyl, 4) isoamyl, 5) n-heptyl, 6) capryl, and 7) decyl alcohols.

The physical constants of the methacrylates we synthesized are listed in Table 1, all the boiling points having been determined at 4 mm, and the specific gravities at 20°, for the sake of convenience.

TABLE 1

No.	Name of methacrylate	Boiling point at 4 mm	Specific gravity at 20°	No.	Name of methacrylate	Boiling point at 4 mm	Specific gravity at 20°
1	Ethyl	19-23°	0.9116	11	Sec-hexyl	56-58°	0.8733
2	n-Propyl	33-36	0.9035	12	n-Heptyl	81-83	0.8843
3	Isopropyl	26-28	0.8869	13	Capryl	84-86	0.8749
4	n-Butyl	39-40	0 8949	14	n-Decyl	117-119	0.8776
5	Isobutyl	36-37	0.8829	15	n-Cetyl	192-195	0.8741
6	Sec-butyl	35-36	0.8844	16	Cyclohexyl	68-70	0.9671
7	n-Amyl	54-57	0.8881	17	Benzyl	95-98	1.0332
8	Isoamyl	49-51	0.8875	18	Diethylene glycol	93-96	1.0499
9	Sec-amyl	42-45	0.8812				
10	n-Hexyl	65-67	0.8849				

A study of the methods of preparing the esters of methacrylic acid showed that it is best to synthesize ethyl, propyl, and isopropyl methacrylates (with yields of 85-90%) by the direct esterification of the respective alcohol and methacrylic acid. The methacrylates from butyl methacrylate upward were best prepared by re-esterifying methyl methacrylate (yields ranging from 80-85%) [2]. All the methacrylates we synthesized were analyzed and found to contain no less than 97-99% of the monomer. The methacrylates were polymerized with 0.5% of benzoyl peroxide. These tests were run in small sealed glass ampoules, which were heated in a thermostat. The following results (Table 2) were secured when the methacrylates were polymerized for 48 hours at 75°, followed by 24 hours at 100°.

The methylcrylate polymers up to C_4 are solid, transparent, colorless,

glasses that are soluble in acetone and benzene, and insoluble in alcohol. The C_5 to C_8 methacrylate polymers are soft, transparent, colorless rubbers that are soluble in organic solvents (with the exception of the alcohols). The polymers of cyclohexyl methacrylate and diethylene glycol methacrylate are produced very quickly, and are transparent, colorless, and insoluble glasses. Decyl methacrylate and cetyl methacrylate are not polymerized under these conditions, while benzyl methacrylate yields a dark, viscous liquid. The methacrylates up to C_7 combine with 5 to 15% of styrene by weight to form copolymers, which can be produced by polymerization in ampoules or in emulsions.

TABLE 2

Polymerization of Methacrylates

No.	Name of methacrylate	Specific viscosity[1] 0.1 m	Specific viscosity[1] 0.01 m	Properties of polymers
1	Ethyl.....	—	0.3733	Solid, hyaline, colorless, transparent, soluble.
2	Isopropyl.....	1.2130	0.0533	
3	n-Butyl.....	—	0.0515	
4	Isobutyl.....	2.3847	0.1345	
5	n-Amyl.....	—	0.1854	Elastic, colorless, transparent, soluble
6	Isoamyl.....	3.3139	0.1965	
7	Sec-amyl.....	—	0.2331	
8	n-Hexyl.....	—	0.1435	
9	Sec-hexyl....	—	0.1848	
10	n-Heptyl.....	—	—	Elastic, colorless, partially soluble, transparent.
11	n-Decyl.....	0.0382	—	Liquid
12	n-Cetyl.....	0.0646	—	
13	Benzyl.....	—	0.0375	Dark viscous liquid
14	Diethylene glycol.....	—	—	Solid, colorless, transparent, insoluble
15	Cyclohexyl....	—	—	Brittle, colorless, transparent, insoluble

SUMMARY

1) The esters of methacrylic acid and the following alcohols have been synthesized: heptyl, sec-amyl, isoamyl, hexyl, sec-hexyl, heptyl, capryl, and decyl alcohols, and their physical constants have been described.

2) Polymerization of various methacrylates has yielded the following polymers: transparent, hyalines up to C_4 and soft, rubbery resins from C_5 to C_8. Decyl methacrylate and cetyl methacrylate did not polymerize.

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Received December 9, 1949.

[1]) The specific viscosity was determined in benzene solutions of the precipitated methacrylate polymers.

THE SYNTHESIS OF RING-SUBSTITUTED DERIVATIVES OF STYRENE

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The investigation of the properties of halogen substitution derivatives of styrene is of considerable theoretical and practical interest; still, there are only a few papers dealing with the synthesis of various halogen substitution derivatives of the styrenes in the literature. Though the bromostyrenes [1] and the chlorostyrenes [2] have been known for a long time, it is not so long ago that the fluorostyrenes were synthesized [3], while the only known iodostyrene [4] is p-iodostyrene. Still less information is available on the polymerizability of various halogen substitution derivatives of the styrenes. We therefore set as our objective the synthesis of a series of halogen substitution derivatives of the styrenes, using various methods of synthesis.

EXPERIMENTAL

I. Synthesis of p-fluorostyrene. Fluorobenzene was prepared from aniline via a diazo compound and a coordination compound with HBF_4 [5]. The fluorobenzene was brominated to convert it into p-fluorobromobenzene, from which we prepared p-FC_6H_4MgBr, which was condensed with acetaldehyde to p-fluorophenylmethylcarbinol, which was then dehydrated with alumina to yield p-fluorostyrene.

160 g of fluorobenzene and 1 g of iron filings were placed in a round-bottomed flask fitted with a reflux condenser, a dropping funnel, and a stirrer, and 88 ml of bromine was added in the course of four hours. Then the mixture was allowed to stand overnight, after which it was heated for three hours over a water bath and the p-fluorobromobenzene was distilled with steam. It was separated from the water, washed with a soda solution and then with water, dried with $CaCl_2$, and distilled. p-Fluorobromobenzene was a colorless liquid with a b.p. of 151-152°, the yield being 255 g (87% of the theoretical).

209 g of p-fluorobromobenzene was reacted with 28.65 g of magnesium in 600 ml of absolute ether to yield a solution of an organomagnesium compound, which was poured into a solution of 52 g of acetaldehyde in 500 ml of absolute ether. The mixture was heated for two hours over a water bath and then set aside to stand overnight. Then the liquid was decomposed with 190 ml of a 25% solution of aluminum chloride (chilled with ice), and the ether layer was separated, washed, dried with $CaCl_2$, and distilled.

p-Fluorophenylmethylcarbinol was a colorless liquid with a b.p. of 104-106° at 20 mm, its yield being 104 g (62% of the theoretical)

Carbinols of this type are usually dehydrated in two ways: 1) with potassium bisulfate and hydroquinone; and 2) with alumina As out tests have shown, the second method yields the better results. A refractory glass tube, with a drawn-out lower end was placed in a vertical tubular furnace, and activated granular alumina was placed within the tube. The carbinol was fed from a dropping funnel (mounted on top of the tube) at the rate of 1 ml per minute. Dehydration was effected at 300-400° and a pressure of 110 mm. The condensate was collected in a receiver that was chilled by dry ice. The resultant p-fluorostyrene was separated from the water, washed with a 5% solution of alkali and a saturated solution of calcium chloride, dried with $CaCl_2$, and distilled in vacuum.

n-Fluorostyrene was a colorless liquid with an aromatic odor, a b.p. of 34-36° (7 mm), and a d_4^{20} 1.029. Its dibromide had a m.p. of 73-75°. It contained 99.7% of the monomer (bromination in CCl_4). The yield was 50% of the theoretical.

II. Synthesis of o-fluorostyrene. Orthotoluidine was converted to orthofluorotoluene (as in the preparation of fluorobenzene), which was oxidized to o-fluorobenzaldehyde by chromyl chloride dissolved in CCl_4. The aldehyde was condensed with malonic acid and pyridine to o-fluorocinnamic acid, which was decarboxylated by heating it with quinoline in the presence of $CuSO_4$ as a catalyst.

A solution of 60 g of o-fluorotoluene (b.p. 114°) in 120 ml of CCl_4 was mixed with a solution of 65 g of chromyl chloride in 120 ml of anhydrous CCl_4, and the reaction mixture was allowed to stand three days at room temperature. Then water was added, the CCl_4 solution of o-fluorobenzaldehyde was washed and dried, and the excess CCl_4 was driven off. The b.p. of o-fluorobenzaldehyde was 70° (20 mm). Its yield was 43 g (63% of the theoretical).

40 g of o-fluorobenzaldehyde, 32.6 g of malonic acid, 8 ml of pyridine, and 56 ml of ethyl alcohol were placed in a flask with a reflux condenser and heated for three days over a water bath. The alcohol was then driven off, the residue crystallizing. The resultant o-fluorocinnamic acid was suction-filtered and recrystallized from alcohol. The yield was 32.5 g (60% of the theoretical). o-Fluorocinnamic acid consisted of colorless crystals with a m.p. of 172-174° (its m.p. is given in the literature as 175° [6] and 178° [3]).

A mixture of 34 g of o-fluorocinnamic acid, 3.4 g of $CuSO_4$ and 68 g of quinoline were placed in a round-bottomed flask, a 50-cm 'herringbone' dephlegmator, a condenser, and a receiver were connected, and the flask was heated over a metallic bath for three hours. Heating was conducted in such a way as to distil most of the liquid at 200-220°. The resultant condensate was treated with 3N HCl, and the o-fluorostyrene was distilled with steam, separated from the water, dried with $CaCl_2$, and vacuum distilled.

o-Fluorostyrene is a colorless liquid with an aromatic odor, a b.p. of 29-30° at 4 mm, and a d_4^{20} 1.0253. It contained 99.75% of the monomer. The yield was 45% of the theoretical

III. Synthesis of o- and p-chlorostyrenes. Ushakov and Matuzov [2] have prepared the chlorostyrenes from the respective toluidines. Walling and Wolfstirn [7] synthesized p-chlorostyrene from p-chlorocinnamic acid. We prepared o-chlorostyrene and p-chlorostyrene, starting with toluene.

The toluene was chlorinated, the resulting mixture of chlorides being separated in a column (efficiency of 15-20 theoretical trays). The fraction that contained the p-chlorotoluene was refined by freezing; the o- and p-chlorotoluenes were oxidized with chromyl chloride, (as in the preparation of o-fluorobenzaldehyde) to o-chlorobenzaldehyde (m.p. 9-10°, yield 60%), which was then condensed (as specified above) with malonic acid to o-chlorocinnamic acid (m.p. 200-201°, 75% yield) and p-chlorocinnamic acid (m.p. 240-242°, 70% yield). Decarboxylation of the chlorocinnamic acids yielded the chlorostyrenes.

p-Chlorostyrene is a colorless aromatic liquid with a b.p. of 53-57° (4 mm), and of 60-62° (6 mm); d_4^{20} 1.0909.

o-Chlorostyrene is a colorless aromatic liquid with a b.p. of 57-58° (5 mm) and of 79-82° (13 mm); d_4^{20} 1.0922. They contained 99.3-99.6% of the monomers. The yield was 50-52% of the theoretical.

IV. Synthesis of the o- and p-bromostyrenes. Shorygin and Shorygina [1] were the first to snythesize p-bromostyrene, starting form p-toluidine. Marvel [8] synthesized p-bromostyrene from p-dibromobenzene. We have snythesized p-bromostyrene in two ways.

1) Synthesis of p-bromostyrene from toluene. The toluene was brominated, the resulting bromides being purified and then fractionated into a column, after which they were further refined by freezing. The crystals of p-bromotoluene we secured had a m.p. of 27-29°. The p-bromotoluene was oxidized with chromyl chloride in CCl_4 (as in the preparation of o-fluorobenzaldehyde), the yield being 61% of the theoretical. The synthesized p-bromobenzaldehyde (m.p. 56-57°) was condensed with malonic acid, yielding p-bromocinnamic acid (m.p. 246-248°, 60% yield). Decarboxylation of the acid yielded p-bromostyrene, the yield being 37.5% of the theoretical.

2) Synthesis of p-bromostyrene from bromobenzene. The bromobenzene was condensed with acetic anhydride in the presence of anhydrous aluminum chloride [9]. The resulting p-bromoacetophenone was reduced to p-bromophenylmethylcarbinol by the V.E. Tishchenko method, using aluminum alcoholate.

90 g of p-bromoacetophenone was dissolved in 500 ml of absolute isopropyl alcohol, 180 ml of a solution of aluminum alcoholate was added, and the whole was heated over a water bath for 6 hours, all the resulting acetone and a large part of the isopropyl alcohol being driven off. The residue was chilled, acidulated with 400 ml of 10% HCl, and extracted with the benzene, the benzene layer being separated, washed, and dried, the benzene driven off, and the residue fractionated in vacuum. p-Bromophenylmethylcarbinol has a b.p. of 144-145° at 20 mm. The yield was 68 g (75.5% of the theoretical). The carbinol was dehydrated with alumina (as in the snythesis of p-fluorostyrene), 65 g of the p-bromophenylmethylcarbinol yielding 28 g of p-bromostyrene (47.5% of the theoretical yield).

p-Bromostyrene is a colorless aromatic liquid with a b.p. of 102° at 20 mm; d_4^{20} 1.3900. It contained 99.6% of the monomer.

Synthesis of o-bromostyrene. We synthesized o-bromostyrene by the same procedure we used for the synthesis of p-bromostyrene, via o-bromocinnamic acid (m.p. 212-214°). o-Bromostyrene is a colorless liquid with an aromatic fragrance, a b.p. of 98° (20 mm) and of 103-104° (22 mm); and d_4^{20} 1.3721. The yield was 35% of the theoretical.

V. Synthesis of p-iodostyrene. Aniline was condensed with acetic anhydride in the presence of zinc chloride, yielding p-aminoacetophenone, which was converted by diazo coupling into p-iodoacetophenone. The latter was reduced with aluminum alcoholate to p-iodophenylmethylcarbinol, which was dehydrated with potassium bisulfate.

A mixture of 100 g of aniline, 250 g of acetic anhydride, and 150 g of anhydrous zinc chloride was boiled for 3-4 hours and then poured into boiling water and neutralized with alkali, throwing down an abundant precipitate. The latter was filtered out, boiled for an hour with concentrated HCl, and neutralized with alkali, the unreacted aniline being driven off with steam. The residue was extracted with ether; driving off the ether caused light-yellow crystals to settle out, which were recrystallized from hot water. The yield was 18 g. p-Aminoacetophenone has a m.p. of 105-106°.

18 ml of concentrated sulfuric acid was added to 21 g of dry p-aminoacetophenone, after which 230 ml of water and 120 g of snow were added, and the whole was diazotized with a solution of 16.3 g of sodium nitrite in 80 ml of water. At the

same time another solution was prepared by heating a mixture of 9.3 g of copper (powder), 16.3 g of iodine, 21 g of potassium iodide, and 27 g of water for an hour and a half. The diazo solution was poured into the warm solution of the copper salt, the resultant p-iodoacetophenone being distilled with steam, separated from the water, and recrystallized from alcohol. The yield was 26 g (48% of the theoretical). p-Iodoacetophenone consists of light-yellow crystals with a m.p. of 85-86°.

The p-iodoacetophenone was reduced to a carbinol with aluminum alcoholate dissolved in isopropyl alcohol (as in the preparation of p-bromophenylmethylcarbinol) 24 g of p-iodoacetophenone yielded a fraction that distilled at 130-140° (3 mm), chilling of which yielded 18 g of the colorless crystals of p-iodophenylmethylcarbinol with a m.p. of 39-40° (the m.p. is given as 40-42° in [4].) The yield was 75% of the theoretical.

The p-iodophenylmethylcarbinol was dehydrated by heating it over a metallic bath at 110 mm pressure with 1% potassium bisulfate and 1% hydroquinone The resulting p-iodostyrene was recrystallized from methanol. The yield was 40% of the theoretical.

p-Iodostyrene consists of minute white crystals with an aromatic odor and a m.p. of 43-44° (the m.p. is given as 44-44.5° in [4]). It contained 99.5% of the monomer.

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Received December 9, 1949.

The Leningrad Institute of Technical Physics of the USSR Academy of Sciences.

THE POLYMERIZATION OF RING-SUBSTITUTED HALOGEN DERIVATIVES OF STYRENE. I.

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Study of the relationship between the chemical structure of substitution derivatives of the styrenes and the polymerizability as well as the properties of the resultant polymers is undoubtedly of theoretical and practical interest. The first researches in this field were carried out by Shorygin and Shorygina [1], who explored o- and p-bromostyrenes, these researches having been repeated much later by foreign investigators [2].

TABLE 1

No	Monomer	b.p. °C	Sp. gr. at 20°
1	o-Fluorostyrene	29–30 (4 mm)	1.0253
2	p-Fluorostyrene	34–36 (7 mm)	1.0290
3	o-Chlorostyrene	57–58 (6 mm)	1.0922
4	p-Chlorostyrene	60–62 (6 mm)	1.0909
5	o-Bromostyrene	98 (20 mm)	1.3721
6	p-Bromostyrene	100–102 (20mm)	1.3900
7	p-Iodostyrene	92–94 (3 mm) m.p. 41–43°	—

TABLE 2

No	Composition of the analyzed mixture	Per cent of the monomer found
1	100% monomer	99.83
2	100% monomer	0.35
3	50% polymer + 50% monomer	50.20
4	75% polymer + 25% monomer	25.62

The synthesis and polymerization of the ortho, meta, and para chlorostyrenes have been investigated in very great detail in a series of papers by Ushakov and Matuzov [3]. The o- and p-fluorostyrenes [4] and p-iodostyrene [5] have been synthesized in recent years. But the literature still contains no systematic research on the polymerization of the homologous series of ring-substituted halogen derivatives of the styrenes. And yet the halogenated styrenes are doubtless worthy of investigation, because of their high polymerizability and the high mechanical and thermal resistance of the polymers, as compared to the polystyrenes.

For our study of the polymerization of the series of ring-substituted halogen derivatives of the styrenes we synthesized the following compounds: 1) o-fluorostyrene, 2) p-fluorostyrene, 3), o-chlorostyrene, 4), p-chlorostyrene, 5), o-bromostyrene, 6), p-bromostyrene, and 7) p-iodostyrene [6]. The constants of the snythesized monomers are given in Table 1.

All the samples of the halogenated styrenes were very pure, containing 99.7 to 99.9% of the monomer. We made a study of the polymerization of all the ring-substituted halogen derivatives of the styrenes at 75, 100, and 125° without a catalyst and at 75° in the presence of 0.05% benzoyl peroxide. The monomers were polymerized in small glass ampoules, which were chilled in dry ice and evacuated in vacuum for a long time before being sealed shut, in order to eliminate all atmospheric oxygen. Series of these sealed ampoules were heated in an oil thermostat with accurate temperature control (±0.05°) and efficient stirring of the liquid. The percentage of the monomer that was not polymerized was determined by brominating it in a carbon tetrachloride solution. Control tests (Table 2) proved that this method was fully suited to the determination of the percentage of the monomer when the polymer was present.

TABLE 3

Polymerization at 75, 100, and 125°

No	Monomer	Temperature	Per cent of polymer after given interval, in hours						
			1	2	3	4	5	6	7
1	Styrene	75°	0.7	—	2.1	—	—	3.7	—
2	o-Fluorostyrene		—	—	—	—	—	7.9	—
3	p-Fluorostyrene		1.1	—	2.5	—	—	4.3	—
4	o-Chlorostyrene		—	—	—	—	—	10.2	—
5	p-Chlorostyrene		1.6	—	3.6	—	—	7.2	—
6	o-Bromostyrene		—	—	—	—	—	7.5	—
7	p-Bromostyrene		1.5	—	3.1	—	—	6.5	—
8	p-Iodostyrene		2.7	—	6.6	—	—	12.4	—
9	Styrene		4.1	—	12.1	—	—	23.3	—
10	p-Fluorostyrene		4.4	—	12.9	—	—	24.4	—
11	p-Chlorostyrene		4.8	—	13.2	—	—	28.1	—
12	p-Bromostyrene		5.0	—	14.0	—	—	26.9	—
13	p-Iodostyrene		7.1	—	18.7	—	—	36.2	—
14	Styrene	100°	2.3	4.8	7.1	—	11.5	—	15.5
15	o-Fluorostyrene		4.1	7.5	13.0	—	21.4	—	29.2
16	p-Fluorostyrene		2.1	4.2	6.5	—	10.3	—	14.7
17	o-Chlorostyrene		5.5	10.2	15.2	—	26.1	—	35.6
18	p-Chlorostyrene		3.5	8.1	12.3	—	20.2	—	27.8
19	o-Bromostyrene		5.1	9.2	13.4	—	22.6	—	31.4
20	p-Bromostyrene		3.3	6.2	8.6	—	14.2	—	20.4
21	p-Iodostyrene		6.1	11.2	16.1	—	26.6	—	37.2
22	Styrene	125°	10.1	19.5	28.5	38.1	46.3	—	—
23	p-Fluorostyrene		9.4	18.3	27.4	36.2	43.8	—	—
24	p-Chlorostyrene		20.4	36.6	54.7	71.1	84.6	—	—
25	p-Bromostyrene		15.5	31.4	44.7	61.5	76.6	—	—
26	p-Iodostyrene		28.2	53.7	83.6	100.	—	—	—

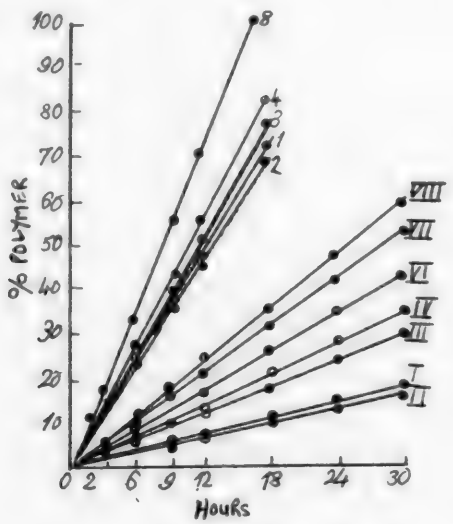

Fig. 1. Polymerization at 75°. I) Styrene, II) p-fluorostyrene, III) p-bromostyrene, IV) p-chlorostyrene, VI) o-bromostyrene, VII) o-chlorostyrene, VIII) p-iodostyrene. 1) Styrene + 0.05% benzoyl peroxide; 2) p-fluorostyrene + 0.05% benzoyl peroxide; 3) p-bromostyrene + 0.05% benzoyl peroxide; 4) p-fluorostyrene + 0.05% benzoyl peroxide; 8) p-iodostyrene + 0.05% benzoyl peroxide.

TABLE 3

Polymerization at 75, 100, and 125°

Per cent of polymer after given interval, in hours							Remarks
9	10	12	14	18	24	30	
5.6	—	7.8	—	11.5	14.2	18.5	No Catalyst
—	—	13.5	—	—	26.1	32.5	
6.0	—	8.1	—	12.2	15.3	19.2	
—	—	21.6	—	—	42.5	53.2	
10.1	—	13.6	—	21.1	27.6	34.7	
—	—	17.4	—	—	34.6	43.3	
8.9	—	12.7	—	18.3	24.2	31.4	
18.5	—	24.1	—	36.3	47.8	59.4	
34.8	—	46.2	—	69.5	—	—	With 0.05% benzoyl peroxide
37.1	—	48.7	—	73.5	—	—	
41.3	—	55.7	—	83.2	—	—	
39.4	—	52.5	—	77.8	—	—	
53.4	—	71.5	—	—	—	—	
—	22.7	—	31.4	39.5	—	—	No Catalyst
—	41.8	—	58.2	73.4	—	—	
—	20.1	—	28.2	35.9	—	—	
—	51.2	—	70.5	89.9	—	—	
—	40.4	—	56.2	70.6	—	—	
—	44.8	—	61.9	79.6	—	—	
—	28.7	—	40.8	51.8	—	—	
—	53.2	—	75.2	95.4	—	—	
—	—	—	—	—	—	—	
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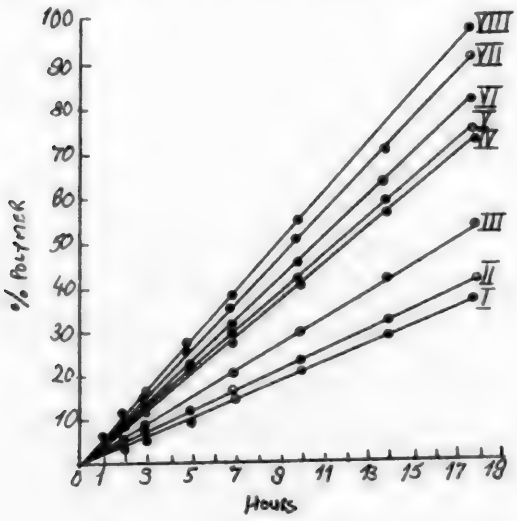

Fig. 2. Polymerization at 100°.
I) Styrene, II) p-fluorostyrene, III) p-bromostyrene, IV) p-chlorostyrene, V) o-fluorostyrene, VI) o-bromostyrene, VII) o-chlorostyrene, VIII) p-iodostyrene.

TABLE 4

Molecular Weight of Polymers

No.	Monomer	Temperature	Polymerization time: 4 hours $\eta_{sp.}$	4 hours mol wt.[1]	5 hours $\eta_{sp.}$	5 hours mol. wt.	7 hours $\eta_{sp.}$	7 hours mol. wt.	9 hours $\eta_{sp.}$	9 hours mol. wt.
1	Styrene	75°	-	-	-	-	-	-	1.1613	64516
2	p-Fluorostyrene	75°	-	-	-	-	-	-	0.6624	36800
3	p-Chorostyrene	75°	-	-	-	-	-	-	0.9577	53205
4	p-Bromostyrene	75°	-	-	-	-	-	-	0.8081	44894
5	Styrene	100°	-	-	-	-	1.2610	70050	-	-
6	o-Fluorostyrene	100°	-	-	-	-	1.0126	56255	-	-
7	p-Fluorostyrene	100°	-	-	-	-	-	-	-	-
8	o-Chlorostyrene	100°	-	-	-	-	0.9409	52272	-	-
9	p-Chlorostyrene	100°	-	-	-	-	0.5196	28866	-	-
10	o-Bromostyrene	100°	-	-	-	-	0.8015	44527	-	-
11	p-Bromostyrene	100°	-	-	-	-	0.1516	8422	-	-
12	Styrene	125°	1.1631	64616	1.2896	71644	-	-	-	-
13	p-Fluorostyrene	125°	0.6986	38811	0.7025	39027	-	-	-	-
14	p-Chlorostyrene	125°	0.5769	32050	0.6127	34038	-	-	-	-
15	p-Bromostyrene	125°	0.6627	36818	-	-	-	-	-	-

[1]) The molecular weights of the precipitated polymers were determined in 0.1 N benzene solutions; Staudinger's formula was employed in the calculations.

TABLE 5[1]

No.	Name	Log A	Activity energy, cal/mol
1	Styrene	10.1	23700
2	p-Bromostyrene	6.3	15300
3	p-Iodostyrene	5.0	14600

[1]) O.V.Kallistov's figures

TABLE 4 (continued)

Molecular Weight of Polymers

Polymerization time								Remarks
12 hours		14 hours		18 hours		24 hours		
η_{sp}	mol. wt.	η_{sp}	mol. wt	η_{sp}	mol. wt.	η_{sp}	mol. wt.	
1.2983	72127	-	-	-	-	2.3508	130600	0.05% benzoyl peroxide
0.8198	45544	-	-	-	-	1.3711	76172	
1.0383	57683	-	-	-	-	2.2654	125855	
0.8809	48938	-	-	-	-	1.0673	59294	
-	-	1 8550	103050	2.4770	137611	-	-	
-	-	1.2401	68894	1.3834	76855	-	-	
-	-	-	-	-	-	0.8105	45027	
-	-	1.0433	57961	1.4511	80616	-	-	
-	-	0.6625	36805	0.7684	42688	-	-	
-	-	0.8582	47677	1.0126	56255	-	-	
-	-	0.2753	15294	0.4931	27394	-	-	
-	-	-	-	-	-	-	-	
-	-	-	-	-	-	-	-	
-	-	-	-	-	-	-	-	
-	-	-	-	-	-	-	-	

TABLE 6

No	Polymer	Softening point, °C, in a capillary
1	Polystyrene	80—82°
2	Polyfluorostyrene (para)	97—104
3	Polychlorostyrene (ortho)	120—135
4	Polychlorostyrene (para)	123—137
5	Polybromostyrene (ortho)	133—140
6	Polybromostyrene (para)	140—153
7	Polyiodostyrene (para)	170—180

As we see in the figures of Table 2, the polymer practically does not interact with the bromine at all under the conditions employed for the determination. Moreover parallel series of dilatometrical tests on the polymerization process also yielded results that agreed with those obtained by the bromination method

The molecular weights of the polymers were determined by precipitating them out of a benzene solution with methanol and drying them to constant weight, after they had first been dissolved in benzene. The polymers of halogenated styrenes are freely soluble in benzene, toluene, xylene. carbon tetrachloride, and chloroform, with the sole exception of the polymer of p-iodostyrene, which dissolves only in chloroform. This polymerization must be compared with the polymerization of styrene to determine the effect of the nature of the halogen introduced into the styrene's benzene ring upon the polymerizability of the halogenated styrene. That is why tests with pure styrene were always run in every series Ushakov and Matuzov [3] had earlier shown that the chlorostyrenes are polymerized more easily than styrene. We have shown that introducing halogen atoms in the styrene s benzene ring makes polymerization occur much faster than in the case of styrene, the polymerization rates depending upon the kind of halogen atom introduced into the monomer. Moreover, the isomerization of the basic molecules of halogenated styrenes exerts a very pronounced effect. As we see from the tables and the graphs, the o-isomers are polymerized faster (1.5 to 2 times faster) than the p-isomers. Furthermore, the molecular weight of the polymers is always much higher in the o-isomers, as had been previously observed by Shorygin [1] and Ushakov [3]. After 18 hours at 100°, for instance, the polymer of o-fluorostyrene had a molecular weight of 76855, while the polymer of p-fluorostyrene had a molecular weight of 45027. After 14 hours at 100° the polymer of o-bromostyrene had a molecular weight of 47677, while that of the polymer of p-bromostyrene was 15294. The halogen atoms, which generally accelerate polymerization, behave differently in this regard (Tables 3 and 4).

Iodine exerts the greatest effect upon the polymerization rate, p-iodostyrene being polymerized faster than the other halogenated styrenes at all temperatures. The polymerization rates of the chlorostyrenes are fairly close to those of the bromostyrenes, though the polymerization rate of o- and p-chlorostyrenes is somewhat higher than that of the o- and p-bromostyrenes. The most pronounced difference in polymerization rates between the ortho and para polymers is observed in the fluorostyrenes, the o-fluorostyrene polymerizing 2 to 2.5 as fast as the p-fluorostyrene. In general, the polymerization rate of p-fluorostyrene is close to that of styrene, proper. At 75° p-fluorostyrene is polymerized somewhat faster than styrene, but at 100 and 125° the polymerization rate of styrene is higher than that of p-fluorostyrene.

The presence of benzoyl peroxide (0.05%) as a catalyst does not change the general order of the polymerization rates of the halogenated styrenes, merely increasing the overall velocity It should be noted, however that when this catalyst is used, the molecular weight of the polymers of p-chlorostyrene rises more than does that of the p-bromostyrene or the p-fluorostyrene. Generally speaking, the molecular weights of the polymers of the halogenated styrenes may be arranged in the following series:

Polyfluorostyrenes > Polychlorostyrenes > Polybromostyrenes

In most instances, the polymers of the p-bromostyrenes have the lowest molecular weights.

All the halogenated styrenes we have investigated may be arranged in the following order of decreasing polymerization rate:

p-I-styrene > o-Cl-styrene > o-Br-styrene > o-F-styrene > n-Cl-styrene > > p-Br-styrene > p-F-styrene

Special tests have made it possible to calculate the activation energies for some of the halogenated styrenes and to compare them with the value found for styrene (Table 5). (Table 5 appears on the bottom of this page.)

These figures indicate that introducing halogen atoms into styrene's benzene ring diminishes the activation energy of the polymerization process. All the polymers of the halogenated styrenes we synthesized were thermoplastic resins of the polystyrene type: transparent, colorless, fairly strong mechanically and with a high softening point that exceeds the softening point of polystyrene [illegible].

SUMMARY

1. A study has been made of the polymerization of ring-substituted halogen derivatives of the styrenes: 1) o-Fluorostyrene, 2) p-fluorostyrene, 3) o-chlorostyrene, 4) p-chlorostyrene, 5) o-bromostyrene, 6) p-bromostyrene, and 7) p-iodostyrene at 75, 100, and 125°.

2. Introducing halogen atoms into the benzene ring of styrene increases the rate at which the substitution derivatives of the styrene are polymerized. p-Iodostyrene exhibits the highest polymerization rate, and p-fluorostyrene the lowest.

3. The ortho isomers possess higher polymerization rates than do the respective para isomers of the halogenated styrenes.

4. Introducing halogen atoms into the benzene ring of styrene lowers the activation energy of polymerization.

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Received December 9, 1949.

TABLE 5[1]

No	Name	Log A	Activation energy, cal/mol
1	Styrene	10.1	23700
2	p-Bromostyrene	6.3	[illegible]
3	p-Iodostyrene	5.0	14690

[1] O.V.Kallistov's figures.

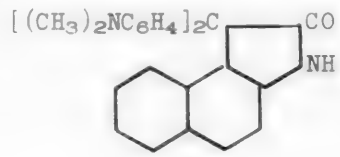
[2] See Consultants Bureau English translation, this issue, page 2043.

THE N-ARYL AMIDES OF HYDROXY CARBOXYLIC ACIDS AND THEIR CONVERSION INTO HETEROCYCLIC COMPOUNDS

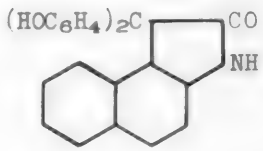
VI. THE STRUCTURE OF THE INTRAMOLECULAR CONDENSATION PRODUCTS OF THE α- AND β-NAPHTHALIDES OF α-HYDROXY CARBOXYLIC ACIDS

P.A.Petyunin

Wichelhaus [1] found that β-naphthisatin reacts with dimethylaniline in the presence of anhydrous zinc chloride and with phenol in the presence of concentrated sulfuric acid, probably yielding 3,3-bis-(4-dimethylaminophenyl)--4,5-benzoxindole (I) in the former case and 3,3-bis-(4-hydroxyphenyl)-4,5--benzoxindole (II) in the second.

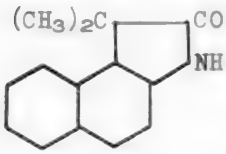


(I)

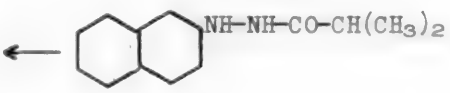


(II)

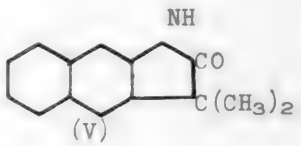
Lieber [2] states that two compounds - 3,3-dimethyl-4,5-benzoxindole (IV) and 3,3-dimethyl-5,6-benzoxindole (V) may be formed by the intramolecular condensation of the β-naphthylhydrazide of isobutyric acid (III):



(IV)



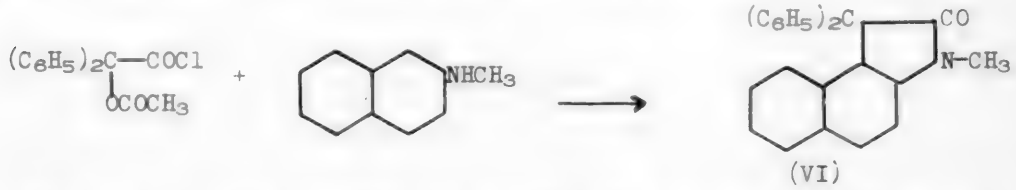
(III)



(V)

Lieber did not learn which of these two formulas represented the structure of 3,3-dimethylnaphthoxindole.

Reeves and Lindwall [3] carried out the following reaction:



(VI)

and assigned the resultant condensation product the structure of 1-methyl-3,3--diphenyl-4,5-benzoxindole (VI). These examples exhaust the references in the literature to the 3,3-diarylsubstitution derivatives of naphthoxindole. None of the authors cited attempted any experimental corroboration of the structural formulas given.

The intramolecular condensation of the naphthalides of α-hydroxy carboxylic acids may be regarded as an intramolecular alkylation with an ortho and para

orienting group in the naphthalene nucleus. As we know, an ortho-para orienting group directs an entering substituent principally into the ring that has no substituent, at the quinogenic position. The α-β-position is more favorable for ortho substitution than the β-β-position. And only after the reactive positions in the first ring are filled does the substituent group enter the new ring chiefly at a quinogenic position [4]. We may expect the formation of two compounds (Diagram A) in the intramolecular condensation of the α-naphthalide of benzilic acid (VII), formula (VIII) having the greater probability. However, the greater three-dimensional proximity of the peri-position and the unsaturated nature of the eight carbon atoms do not exclude the possibility of a peri-condensation and the formation of the compound (IX).

Before choosing between these formulas we had to demonstrate that a peri-condensation was feasible. We did this by first introducing a substituent at the most reactive position, so that a peri-condensation became naturally possible. Thus, by reacting the ethyl ester of α-naphthyloxamic acid (XII) with bromine in pyridine we got the ethyl ester of 2,4-dibromo-1-naphthyloxamic acid (XIII), which was saponified, yielding the 2,4-dibromonaphthylamine-1 (XIV) described in the literature (Diagram B). The action of phenylmagnesium bromide upon (XIII) yielded the 2,4-dibromo-1-naphthalide of benzilic acid (XV). The latter yielded the peri-condensation product (XI) when reacted with concentrated sulfuric acid.

DIAGRAM A

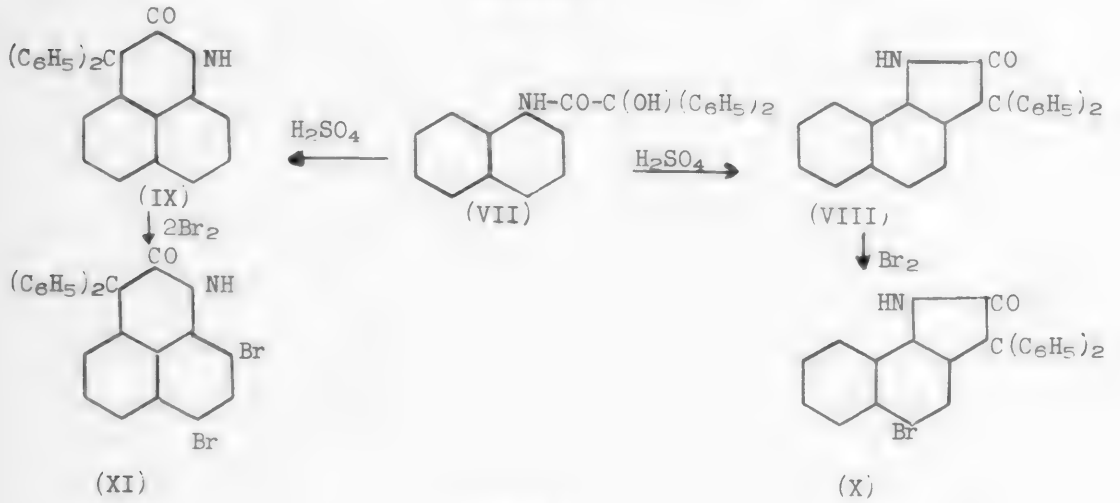
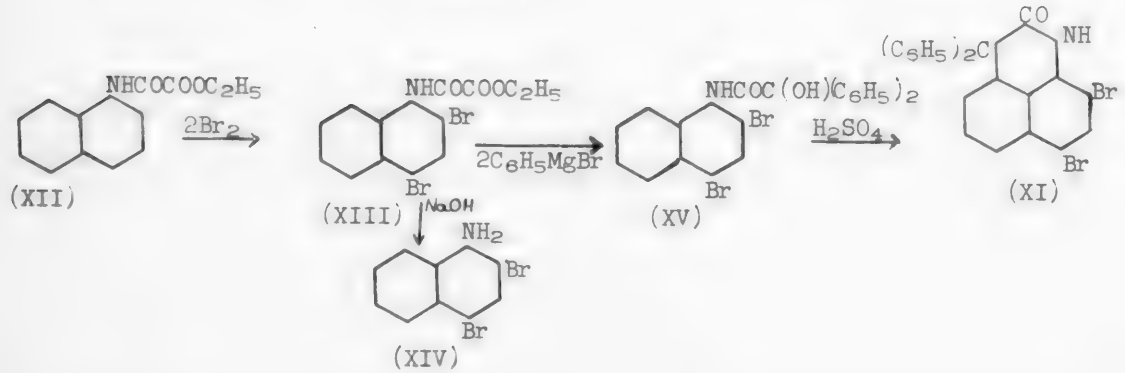
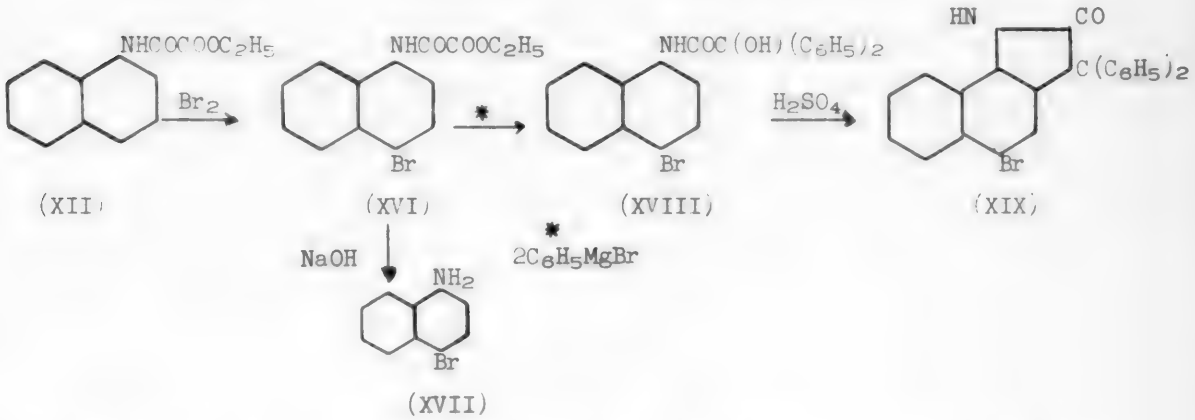


DIAGRAM B



The choice between the formulas (VIII) and (IX) was made after a study of the bromination of the product of the intramolecular condensation of the α--naphthalide of benzilic acid. Bromination was carried out in pyridine, the reaction being based upon introduction of two atoms of bromine. In this case one atom of bromine could be introduced into the compound (VIII), yielding (X), and two atoms of bromine into (IX), since it had two reactive positions, yielding (XI). This yielded a substance that contained one atom of bromine, the structure of which was established as follows:

DIAGRAM C



The action of bromine upon the ethyl ester of α-naphthyloxamic acid (XII) yielded the substance (XVI), which yielded the well-known 4-bromonaphthylamine-1 (XVII) when it was heated with a concentrated alkali. The action of phenylmagnesium bromide upon the ethyl ester of 4-bromo-1-naphthyloxamic acid (XVI) yielded the corresponding aryl amide (XVIII), while treating the latter with concentrated sulfuric acid yielded 5-bromo-3,3-diphenyl-6,7-benzoxindole (XIX). The identity of (X) and (XIX) was established by the melting point of a mixed fusion sample. Moreover, the physical constants likewise were evidence against any peri-condensation: the high m.p. of 282° for (X), which contained 1 atom of bromine, did not agree with the lower m.p. of 246-247° for the peri-condensation product (XI), which contained two bromine atoms.

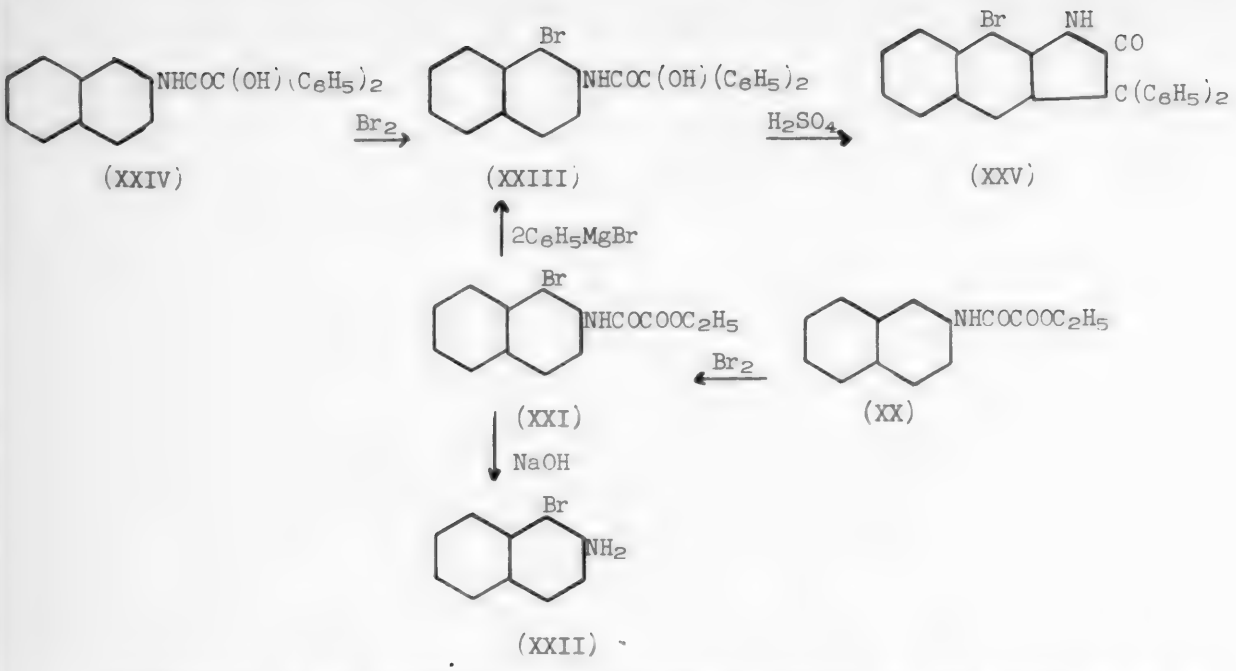
We may therefore take it as established that the α-naphthalides of a-hydroxy acids enter into an α-β condensation, a peri-condensation taking place if the β-position is occupied We have demonstrated that a β-β condensation is feasible for the β-naphthalides of α-hydroxy acids (Diagram D).

When an acetic-acid solution of the ethyl ester of β-naphthyloxamic acid (XX)was reacted with bromine, we secured the ethyl ester of 1-bromo-2-naphthyloxamic acid (XXI), which yielded the well-known 1-bromonaphthylamine-2 (XXII) when it was heated with a concentrated alkali. The reaction of (XXI) with phenylmagnesium bromide yielded the 1-bromo-2-naphthalide of benzilic acid (XXIII). The same compound was synthesized by reacting an acetic-acid solution of the β-naphthalide of benzilic acid (XXIV) with bromine.

Treating (XXIII) with concentrated sulfuric acid yielded the β-β condensation product — 3,3-diphenyl-7-bromo-5,6-benzoxindole (XXV). The intramolecular condensation of the β-naphthalide of benzilic acid (XXIV) may result in the formation of the two compounds (Diagram E).

We chose between these two formulas after a study of the

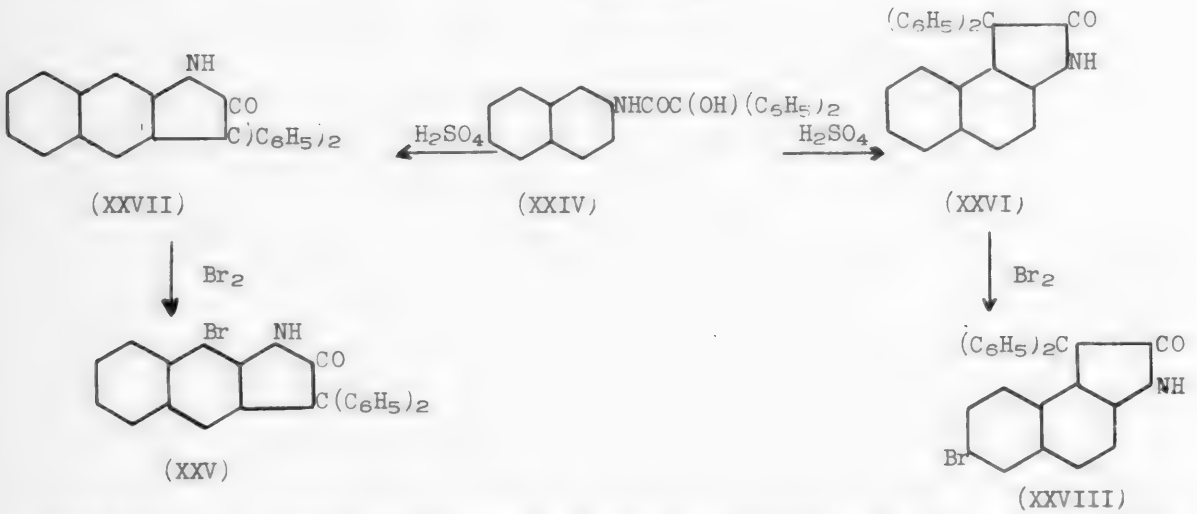
DIAGRAM D



bromination of the intramolecular condensation product of the β-naphthalide of benzilic acid.

Compound (XXVII) has the most reactive free position at the α-carbon atom, so that it ought to yield the compound (XXV) already described by us when reacted

DIAGRAM E



with bromine. Compound (XXVI) ought to yield a substance hitherto not described in the literature. This bromination yielded a new substance, which may be assigned the structure of 3,3-diphenyl-6-bromo-β-naphthoxindole (XXVIII) on the basis of the

order in which the hydrogen atoms in the β-naphthylamine nucleus are replaced [5].

Hence, the β-naphthalides of α-hydroxy acids enter into an α-β condensation, a β-β condensation being feasible only when the α position is already occupied.

EXPERIMENTAL

Ethyl ester of 1-bromo-2-naphthyloxamic acid (XXI). A solution of 4 g of bromine in 6 ml of glacial acetic acid was added to 6 g of the ethyl ester of β-naphthyloxamic acid dissolved in 30 ml of glacial acetic acid. The reaction product was recovered in the usual manner. It crystallized from alcohol as colorless needles with a m.p. of 99.5-100.5°. The yield was 6.5 g, or 81.2% of the theoretical.

0.1021 g substance: 0.0599 g AgBr. Found %: Br 24.96. $C_{14}H_{12}O_3NBr$. Calculated %: Br 24.83.

0.7 g of the ethyl ester of 1-bromo-2-naphthyloxamic acid was heated for 10-15 minutes with 4 ml of a 50% solution of potassium hydroxide. The resultant oil crystallized upon cooling. Crystallization from dilute alcohol yielded colorless needles with a m.p. of 63°, which agrees with the figure given in the literature for 1-bromonaphthylamine-2 [6].

The ethyl ester of 1-bromo-2-naphthyloxamic acid has not been described in the literature.

Ethyl ester of 2,4-dibromo-1-naphthyloxamic acid (XIII). 2 g of the finely pulverized ethyl ester of α-naphthyloxamic acid was added to a solution of 3 g of bromine in 10 ml of pyridine. The reaction mass warmed up considerably, the α-naphthyloxamate dissolving. After the reaction mass had stood for four hours at room temperature, it was diluted with water, and the resultant oil crystallized. The substance was insoluble in water, but dissolved in organic solvents. It crystallized from alcohol as colorless needles with a m.p. of 189°. The yield was 2 g, or 60.6% of the theoretical.

0.1322 g substance: 0.1230 AgBr. Found %: Br 39.65. $C_{14}H_{11}O_3NBr_2$. Calculated %: Br 39.87.

Heating it with a 50% solution of potassium hydroxide yielded 2,4-dibromonaphthylamine-1. M.P. 118° [7].

The ethyl ester of 2,4-dibromo-1-naphthyloxamic acid has been synthesized for the first time by us.

Ethyl ester of 4-bromo-1-naphthyloxamic acid (XVI). Initial substances: a solution of 10 g of the ethyl ester of α-naphthyloxamic acid in 80 ml of glacial acetic acid, and 13.8 g of bromine. The ester was insoluble in water or diethyl ether, but was soluble in the other common solvents. It crystallized from alcohol as colorless needles with a m.p. of 136.5°. The yield was 7 g, or 60% of the theoretical.

0.1428 g substance: 0.0830 g AgBr. Found %: Br 24.73. $C_{14}H_{12}O_3NBr$. Calculated %: Br 24.83.

Heating it with a 50% solution of potassium hydroxide yielded 4-bromonaphthylamine-1. M.p. 102° [7].

The ethyl ester of 4-bromo-1-naphthyloxamic acid has not been described in the literature.

4-Bromo-1-naphthalide of benzilic acid (XVIII). The following were used in

this reaction: 3 g of the ethyl ester of 4-bromo-1-naphthyloxamic acid, 7 g of bromo-benzene, and 1.08 g of magnesium. The substance was insoluble in water or gasoline, slightly soluble in ether and carbon tetrachloride, and freely soluble in alcohol, benzene, and acetic acid. Concentrated sulfuric acid colored it a transitory brown. It crystallized from acetic acid as colorless needles with a m.p. of 177°. The yield was 3.1 g, or 77.1% of the theoretical.

0.1306 g substance: 0.0564 g AgBr; 0.2103 g substance: 0.0910 g AgBr. Found %: Br 18.37, 18.41. $C_{24}H_{18}O_2NBr$. Calculated %: Br 18.5.

The 4-bromo-1-naphthalide of benzilic acid has not been described in the literature.

2,4-Dibromo-1-naphthalide of benzilic acid (XV). Initial substances: 4 g of the ethyl ester of 2,4-dibrimo-α-naphthyloxamic acid, 9.4 g of bromobenzene, and 1.4 g of magnesium. The naphthalide was insoluble in water, ether or gasoline, but was soluble in alcohol, benzene, acetic acid, toluene, and chloroform. It crystallized from acetic acid as colorless platelets with a m.p. of 214.5°. Concentrated sulfuric acid colored it a transitory brown. The yield was 4.7 g, or 94% of the theoretical.

0.1104 g substance: 0.0808 g AgBr; 0.0932 g substance: 0.0686 g AgBr. Found %: Br 31.14, 31.31. $C_{24}H_{17}O_2NBr_2$. Calculated %: Br 31.29.

1-Bromo-2-naphthalide of benzilic acid (XXIII). a) The following substances were used in the reaction: 3.2 g of the ethyl ester of 1-bromo-2-naphthyloxamic acid 9.4 of bromobenzene, and 1.4 g of magnesium. The naphthalide was insoluble in water or gasoline, slightly soluble in alcohol and acetic acid, and readily soluble in chloroform and dichloroethane. Concentrated sulfuric acid colored it a transitory red-brown. It crystallized from glacial acetic acid as colorless needles with a m.p. of 186°. The yield was 2.6 g, or 40.3% of the theoretical.

b) 1.55 g of the β-naphthalide of benzilic acid was dissolved in 50 ml of glacial acetic acid. A solution of 0.7 g of bromine in 4 ml of glacial acetic acid was added to the resultant solution. The reaction product was recovered as indicated above. The yield was 1.8 g, or 94.7% of the theoretical. It crystallized from glacial acetic acid as colorless needles with a m.p. of 186°. A sample mixed with the product of the action of phenylmagnesium bromide upon the ethyl ester of 1-bromo-2-naphthyloxamic acid fused without any depression of the melting point.
0.1044 g substance: 0.0450 g AgBr; 0.1830 g substance: 0.0792 g AgBr. Found %. Br 18.34 18.41. $C_{24}H_{18}O_2NBr$. Calculated %: Br 18.5
The 1-bromo-2naphthalide of benzilic acid has not been described in the literature.

3,3-Diphenyl-5-bromo-6,7-benzoxindole (X). (3,3-Diphenyl-5-bromo-α-naphthoxindole.) a) Initial substances: 1.2 g of the 4-bromo-1-napthalide of benzilic acid, dissolved in 20 ml of glacial acetic acid, and 3 ml of concentrated sulfuric acid. This yielded 1.1 g of an air-dry product, or 96% of the theoretical yield. The product was insoluble in water, slightly soluble in alcohol and carbon tetrachloride, and more soluble in acetic acid and benzene. It crystallized from acetic acid as colorless needles with a m.p. of 282°.

0.1130 g substance: 0.0510 g AgBr; 0.1221 g substance: 0.0549 g AgBr Found %: Br 19.2, 19.13. $C_{24}H_{16}ONBr$. Calculated %: Br 19.3.

3,3-Diphenyl-5-bromo-α-naphthoxindole has not been described in the literature.

b) 7 g of finely crushed 3,3-diphenyl-α-naphthoxindole was added to a solution of 1.2 g of bromine (a 25% excess over the theoretical quantity required for the

introduction of 2 bromine atoms) in 10 ml of pyridine. This yielded 1.2 g, or 97% of the theoretical, based on a monobrominated compound It crystallized from acetic acid as colorless needles with a m.p. of 282°.

A fusion sample mixed with the intramolecular condensation product of the 4-bromo-1-naphthalide of benzilic acid fused without any depression of the melting point.

Lactam of 1-amino-2,4-dibromonaphthyl-(8)-diphenylacetic acid (XI). 30 ml of concentrated sulfuric acid was added to a solution of 1.4 g of the 2,4-dibromo-1-naphthalide of benzilic acid in 30 ml of glacial acetic acid. The brown coloration turned light-yellow after the mixture had stood for some time. The yield was 1.3 g, or 96.3% of the theoretical. The product was insoluble in water or ether, slightly soluble in alcohol, and readily soluble in chloroform, benzene, toluene, and acetic acid. It crystallized from acetic acid as a colorless crystalline powder with a m.p. of 246-247° (with decomposition).

0.0776 g substance: 0.0589 g AgBr: 0.1112 g substance: 0.0848 g AgBr. Found %: Br 32.29, 32.45. $C_{24}H_{15}ONBr_2$. Calculated %: Br 32.43.

The lactam of 1-amino-2,4-dibromonaphthyl-8-diphenylacetic acid has not been described in the literature.

3,3-Diphenyl-7-bromo-5,6-benzoxindole (XXV). The following substances were used for the reaction: a solution of 2 g of the 1-bromo-2-naphthalide of benzilic acid in 40 ml of glacial acetic acid, and 20 ml of concentrated sulfuric acid. The red-brown coloration of the mixture turned a light-yellow, and the reaction product was recovered in the usual manner The yield was 1.75 g, or 91.1% of the theoretical. The substance was insoluble in water, gasoline or ether, slightly soluble in alcohol and acetic acid, and readily soluble in benzene. It crystallized from a large quantity of glacial acetic acid as colorless hexagonal platelets with a m.p. of 293-295° (with decomposition).

0.1424 g substance: 0.0640 g AgBr: 0.1304 g substance: 0.0590 g AgBr. Found %: Br 19.12, 19.25. $C_{24}H_{16}ONBr$. Calculated %: Br 19.3.

3 3-Diphenyl-7-bromo-5,6-benzoxindole has not been described in the literature.

3,3-Diphenyl-6-bromo-β-naphthoxindole (XXVIII). 1 g of 3,3-diphenyl-β-naphthoxindole was dissolved in 40 ml of glacial acetic acid, and 0.6 g of bromine was added. When the reaction was complete, the product was isolated as in the analogous experiments described. It crystallized from acetic acid as colorless needles with a m.p. of 304-305° (with decomposition). The yield was 0.8 g, or 64.5% of the theoretical. The substance was insoluble in water, slightly soluble in alcohol, and freely soluble when heated in acetic acid, benzene, toluene, and chloroform.

0.1415 g substance: 0.0636 g AgBr: 0.0980 g substance: 0.0442 g AgBr. Found %: Br 19.12, 19.19. $C_{24}H_{16}ONBr$. Calculated %: Br 19.3.

3,3-Diphenyl-6-bromo-β-naphthoxindole has not been described in the literature

SUMMARY

1) It has been found that the intramolecular condensation of the α-naphthalides of α-hydroxy carboxylic acids yields α-β condensation products, peri-condensation products being formed when the β position is occupied.

2) The β-naphthalides of α-hydroxy carboxylic acids likewise yield α-β

condensation products, β-β condensation products being formed only when the α position is occupied.

3) Several bromine derivatives of α and β naphthyloxamates, α- and β-naphthalides of benzilic acid, 3,3-diphenyl-α- and β-naphthoxindoles, and other compounds not hitherto described in the literature have been synthesized and their properties described.

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Received October 13, 1949.

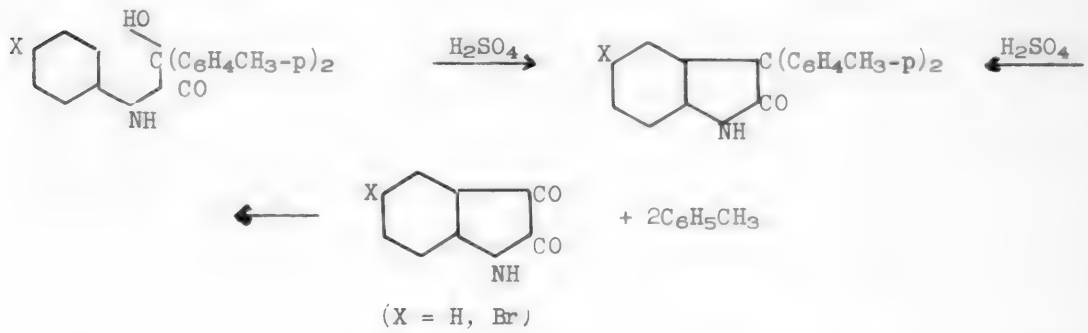
THE N-ARYL AMIDES OF HYDROXY CARBOXYLIC ACIDS AND THEIR CONVERSION INTO HETEROCYCLIC COMPOUNDS

VII. INTRAMOLECULAR CONDENSATION OF THE ARYL AMIDES OF p,p-DITOLYLGLYCOLIC ACID

P. A. Petyunin and I. S. Berdinksy

By reacting concentrated sulfuric acid with acetic-acid solutions of the anilide and the p-bromanilide of p,p-ditolylglycolic acid we have synthesized substances whose melting points correspond to those described in the literature for 3,3-di-(p)-tolyl-5-bromoxindole [2]. We repeated the synthesis of these compounds by the Baeyer method, the mixed melting point exhibiting no depression

The foregoing may be illustrated by the following diagram·



(X = H, Br)

Hence, the action of concentrated sulfuric acid converts the aryl amides of p,p-ditolylglycolic acid into the corresponding derivatives of 3,3-di-(p)-tolyloxindole.

In addition to the examples mentioned, we also effected the following intramolecular condensation:

$$Ar - NH - CO - C(OH)(C_6H_4CH_3\text{-}p)_2,$$

where

Ar = p-$CH_3C_6H_4$- p-$C_2H_5OC_6H_4$-, o-$CH_3OC_6H_4$- α-$C_{10}H_7$- and β-$C_{10}H_7$-.

The properties of the synthesized compounds are listed in Table 1.

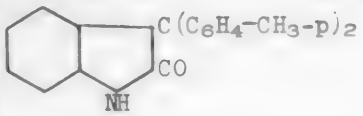
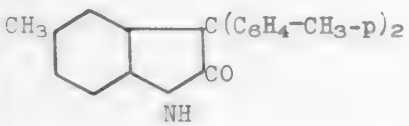
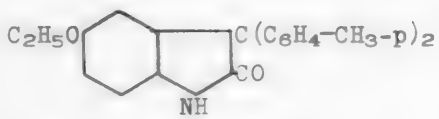
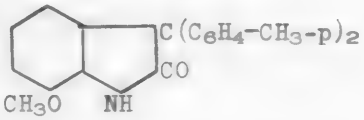
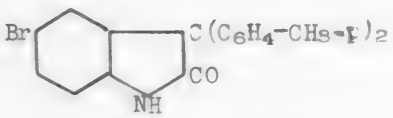
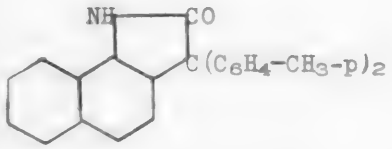
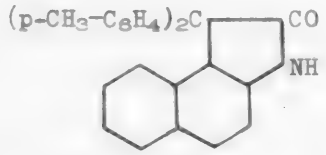
Variation of the optimum quantity of sulfuric acid with the reaction temperature.

These tests were run with a 0.9% solution of the α-naphthalide of p,p-ditolylglycolic acid in acetic acid.

A solution of the α-naphthalide of p,p-ditolylglycolic acid was heated to the desired temperature and concentrated sulfuric acid was then added drop by drop from a buret until a crimson coloration no longer appeared. The amount of sulfuric acid consumed was recorded as the optimum quantity. The results are depicted graphically in Figure 1.

TABLE 1

3,3-Di-p-tolyloxindole and Its Derivatives

No	Formula	Melting point
1		200-201°[1]
2		201
3		263
4		225
5		235[2]
6		220
7		246.5

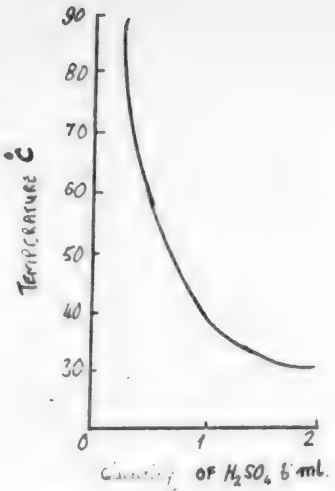


Fig.1. Effect of reaction temperature upon the optimum quantity of sulfuric acid.

We see in Figure 1 that the quantity of sulfuric acid required for the condensation drops sharply as the reaction temperature is raised.

Variation of the optimum quantity of sulfuric acid with the structure of the aryl amide of a hydroxy carboxylic acid.[3] We determined this variation by measuring the optimum quantities of sulfuric acid required for aryl amides that differed in the structure of the radical attached to the nitrogen atom and to the carbinol carbon. The tests were run at the same molar concentration of the substance (0.025 mol per liter of acetic acid)[4] and at identical temperatures (20°).

We see that introducing alkyl groups into the phenyl radicals attached to the

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[1]) M.p. given as 200° in the literature [1].

[2]) M.p. given as 235° in the literature [2].

[3]) Henceforth we shall call the aryl amides of hydroxy carboxylic acids simply aryl amides.

[4]) Glacial acetic acid was employed throughout.

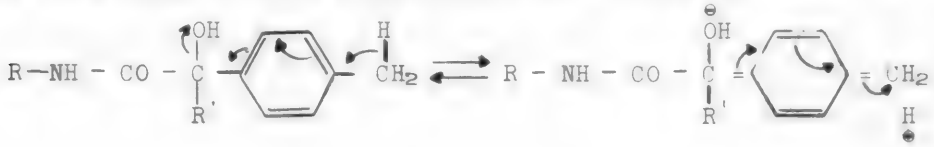
TABLE 2

Effect of the Structure of Aryl Amides on the Optimum Quantity of Sulfuric Acid

No.	Aryl amide formula	Quantity of conc. H_2SO_4, ml
1	$C_6H_5NH-CO-C(OH)(C_6H_5)_2$	3.5
2	$p-CH_3C_6H_4NH-CO-C(OH)(C_6H_5)_2$	3.5
3	$o-CH_3OC_6H_4NH-CO-C(OH)(C_6H_5)_2$	3.5
4	$\alpha-C_{10}H_7NH-CO-C(OH)(C_6H_5)_2$	3.5
5	$\beta-C_{10}H_7NH-CO-C(OH)(C_6H_5)_2$	3.5
6	$p-C_2H_5OC_6H_4-NH-CO-C(OH)(C_6H_4CH_3-p)_2$	2.0
7	$p-CH_3C_6H_4NH-CO-C(OH)(C_6H_4CH_3-p)_2$	1.5
8	$o-CH_3OC_6H_4NH-CO-C(OH)(C_6H_4CH_3-p)_2$	1.5
9	$\alpha-C_{10}H_7NH-CO-C(OH)(C_6H_4CH_3-p)_2$	2.5
10	$\beta-C_{10}H_7NH-CO-C(OH)(C_6H_4CH_3-p)_2$	2.4

carbinol carbon (the aryl amides 6-10) lowers the amount of sulfuric acid required for condensation. Introducing the same substituent groups in the radical attached to the nitrogen (aryl amides 1-5) has no effect.

Owing to the partial dissociation of the hydrogen in the methyl group, the electrons of the benzene ring are shifted toward the central carbon atom, which should be reflected in an increase in basic properties and, hence, in a decrease in the amount of sulfuric acid required for condensation, since the latter takes place via a stage in which a halochromic salt is formed.



The substituent groups in the radical attached to the nitrogen atom cannot exert a similar influence, inasmuch as they are not attached to the central carbon atom by a conjugated chain.

Influence of the nature of the radical attached to the nitrogen atom upon the condensation rate. In these tests we employed the following aryl amides:

$ArNH-CO-C(OH)(C_6H_5)_2$ (Ar = C_6H_5-, p-$CH_3C_6H_4$- and o-$CH_3OC_6H_4$-)
$Ar'NH-CO-C(OH)(C_6H_4CH_3-p)$ (Ar' = C_6H_5-, p-$C_2H_5OC_6H_4$-, o-$CH_3OC_6H_4$- m-$CH_3OC_6H_4$-).

The tests were run with solutions of 0.025 mol of the aryl amide in 1 liter of acetic acid. The individual runs were made with 1 ml of this solution. The optimum quantities of sulfuric acid were used, as determined for each aryl amide at 20°.

We believe that citing the data for the aryl amides of benzoic acid [Fig. 2] suffices to describe the effect of the structure of the radical attached to the nitrogen atom upon the condensation rate. The +M-effect of the NHAc group in ortho positions of the benzene ring increases the electron density, which is

a necessary prerequisite for condensation. The introduction of substituents into the benzene ring attached to the nitrogen atom may hinder or promote this polarization. In compounds that contain electron donor groups in the ortho or para positions the orienting effects of the substituent groups are in competition. In intermolecular processes the reaction would follow the line of the strongly orienting group. In intramolecular reactions, however, there is only a limited choice of positions open for the reaction. The carbon atoms whose electron densities may be lower than those of others, but are sterically more favorable, may enter into the reaction.

The data cited indicate that substituents in the ortho and para positions to the NHAc group cause no significant changes in the condensation rate, or else this influence is so slight as to be practically negligible.

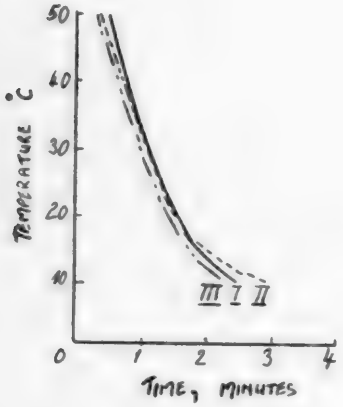


Fig.2. Variation of the condensation rate with the nature of the radicals attached to the nitrogen atom. [1]

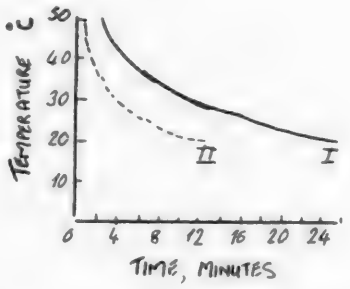


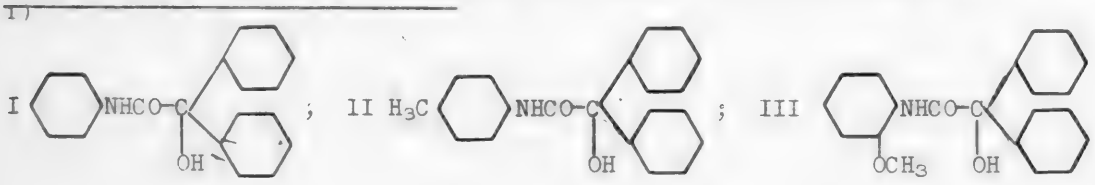
Fig.3. Curves of the condensation rates of the ortho and meta anisides of p-tolilic acid.
1) Ortho aniside; 2) meta aniside.

When a metnoxy group is introduced at the meta position to the NHAc group, its +M-effect increases the electron density at the points of reaction, and, as our tests have shown [Fig. 3], the m-aniside of p-tolilic acid is condensed faster than its isomer.

The accelerating effect of a meta substituent has been described in other cases such as an azo coupling reaction [3].

Influence of the nature of the radicals attached to the carbinol carbon atom upon the condensation rate. This was determined by measuring the condensation rates for aryl amides the structure of whose radicals attached to the carbinol carbon atom differed. The following aryl amides were investigated:

1)



$ArNH-CO-C(OH)AR_2'$, where Ar = C_6H_5-, o-$CH_3OC_6H_4-$, p-$C_2H_5OC_6H_4-$, p-$CH_3C_6H_4-$, α-$C_{10}H_7-$ and β-$C_{10}H_7-$; Ar' = C_6H_5- p-$CH_3C_6H_4-$.

Our results reflect a regular behavior pattern, and we believe we may confine ourselves to reproducing two graphs [Figs. 4 and 5] by way of describing the pattern.

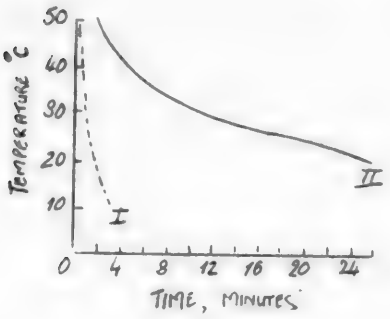


Fig.4. Curves of the condensation rates of anilides of benzilic and p-tolilic acids
I) Benzilanilide; II) p-tolilanilide.

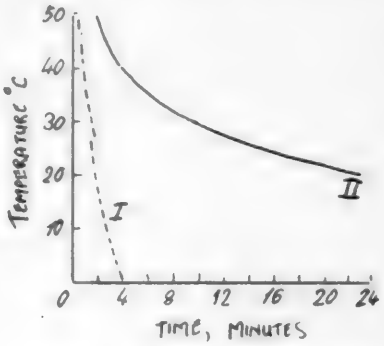


Fig.5. Curves of the condensation rates of the ortho anisides of benzilic and p-tolilic acids.
I) Benzil-o-aniside; II) p-tolil-o-aniside.

Introducing substituent groups in the radicals attached to the carbinol carbon atom greatly affects the condensation rates of aryl amides of α-hydroxy carboxylic acids. When p-tolil groups are substituted for the phenyl ones, the condensation rate is diminished by a factor 15 to 20.

EXPERIMENTAL

Ethyl ester of m-methoxyoxanilic acid. 11.5 g of m-anisidine and 19 g of ethyl oxalate were boiled together for 3 hours over a sand bath. This yielded 2 g of the di-(m)-aniside of oxalic acid, recrystallized from glacial acetic acid. M.p. 183°. The substance was insoluble in water or alcohol, but soluble when heated in toluene, chloroform, and acetic acid.

0.0923 g substance: 12.05 ml 0.05 N. H_2SO_4. Found %: N 9.14. $C_{16}H_{16}O_4N_2$. Calculated %: N 9.33.

The ethyl ester of m-methoxyoxanilic acid was insoluble in water and only slightly soluble in the other organic solvents. It crystallized from alcohol as colorless needles with a m.p. of 97°. The yield was 12.7g, or 68.69% of the theoretical.

0.3272 g substance: 28.2 ml 0.05 N H_2SO_4; 0.2064 g substance; 18.8 ml 0.05 N H_2SO_4. Found %: N 6.03, 6.37. $C_{11}H_{13}O_3N$. Calculated %: N 6.28.

We are the first to have synthesized the di-(m)-aniside of oxalic acid and the ethyl ester of m-methoxyoxanilic acid.

m-Methoxyoxanilic acid. 1 g of the ethyl ester of m-methoxyoxanilic acid was heated in 20 ml of 10% sodium hydroxide solution until it dissolved. The reaction mass was acidulated with sulfuric acid until its reaction was acid with Congo red, and the reaction product was recovered in the usual manner. The substance dissolved when heated in water; it was freely soluble in organic solvents. M.p. 168° (with decomposition). The yield was 0.6 g, or 63.73% of the theoretical.

0.1302 g substance : 13 1 ml 0 05 N H_2SO_4. Found %: N 7.04. $C_9H_9O_4N$ Calculated%: N 7.18.

m-Methoxyoxanilic acid is not described in the literature.

m-Methoxyoxanilamide. A solution of 1.2 g of the ethyl ester of m-methoxyoxanilic acid in 15 ml of alcohol was saturated with gaseous ammonia. The amide was insoluble in water, slightly soluble in alcohol and toluene, and readily soluble in acetic acid It crystallized from alcohol as colorless needles with a m p. of 173 5°. The yield was 0.9 g of the substance or 87.36% of the theoretical.

0.3386 g substance: 68.7 ml 0.05 N H_2SO_4; 0.1741 g substance : 18 77 ml 0.05 N H_2SO_4. Found %: N 14.2, 14.02. $C_9H_{10}O_3N_2$. Calculated %: 14 44.

m-Methoxyoxanilamide is not described in the literature.

The p-phenetide of p,,p-ditolylglycolic acid. The following were used for the reaction: 5.9 g (1 mol) of the ethyl ester of p-ethoxyoxanilic acid, 27 g (5 mols) of p-iodotoluene, and 3 g of magnesium The yield was 8.1 g, or 87% of the theoretical.

The phenetide was insoluble in water, though freely soluble in most organic solvents. It turned a transitory cherry-red when reacted with concentrated sulfuric acid. It crystallized from alcohol as needles gathered in clusters. M.p. 115.5-116.5°.

0.2830 g substance: 7.3 ml 0.1 N H_2SO_4. Found %: N 3.61. $C_{24}H_{25}O_3N$. Calculated %: N 3.73.

The p-phenetide of p-p-ditolylglycolic acid is not described in the literature.

o-Aniside of p,p-ditolylglycolic acid. Initial substances: 8.2 g of ethyl o-methoxyoxanilate, 25 5 g of p-bromotoluene, and 4 g of magnesium. The yield was 11.8 g, or 88 7% of the theoretical The aniside was insoluble in water, slightly soluble in ether and readily soluble in alcohol, toluene, and benzene. It dissolved in concentrated sulfuric acid, turning the latter cherry-red, which turned crimson, and then orange, turning light-yellow when gently heated. It was crystallized from toluene as colorless needles. M.p. 181.5 - 182.5°.

0.2727 g substance: 7.3 ml 0.1 N H_2SO_4. Found %: N 3.75. $C_{23}H_{23}O_3N$. Calculated %: N 3.88

The o-aniside of p-tolilic acid is not described in the literature.

p-Toluide of p,p-ditolylglycolic acid. The p-toluide of p-tolilic acid was prepared from 7 7 g of the ethyl ester of p-methyloxanilic acid, 4 g of magnesium, and 25.5 g of p-bromotoluene. This yielded 9 4 g of the substance, or 72% of the theoretical yield The toluide was insoluble in water, gasoline, or dichloroethane, slightly soluble in benzene and chloroform, and readily soluble in alcohol and acetic acid It dissolved in concentrated sulfuric acid, turning the latter reddish-purple, which gradually disappeared. It crystallized from dilutealcohol as colorless needles with a m.p. of 131-133°.

0.1996 g substance: 5.6 ml 0.1 N H_2SO_4. Found %: N 3.93. $C_{23}H_{23}O_2N$. Calculated %: N 4.06

The p-toluide of p,p-ditolylglycolic acid is not described in the literature.

p-Bromanilide of p,p-ditolylglycolic acid. A solution of 1.5 g of bromine in 6 ml of acetic acid was added to a solution of 3.3 g of ditolylglycolanilide in 35 ml

of acetic acid. When the reaction was complete, the contents of the flask were poured into 100 ml of water. The resulting precipitate was crystallized from alcohol. Colorless needles with a m.p. of 151°. The yield was 3.6 g, or 87.8% of the theoretical.

The anilide was insoluble in water, slightly soluble in alcohol and acetic acid, readily soluble in chloroform and dichloroethane. It colored concentrated sulfuric acid a transitory crimson.

0.1171 g substance: 0.5300 g ArBr. Found %: Br 19.26. $C_{22}H_{20}O_2NBr$. Calculated %: Br 19.47.

The position of the bromine was established by converting the p-bromanilide into the well-known oxindole derivative of 5-bromo-p-toluisatin.

The p-bromanilide of p,p-ditolylglycolic acid is not described in the literature.

m-Aniside of p,p-ditolylglycolic acid. Initial substances: 2.2 g of the m-methoxyoxanilate, 13 g of p-iodotoluene, and 1.4 g of magnesium. The aniside was insoluble in water, slightly soluble in benzene and gasoline, and readily soluble in the other organic solvents. It imparted a transient crimson color to concentrated sulfuric acid. It crystallized slowly from benzene as colorless platelets with a m.p. of 116°. The yield was 1.5 g, or 40.5% of the theoretical.

0.1501 g substance: 8.2 ml 0.05 N H_2SO_4; 0.1427 g substance : 7.7 ml 0.05 N H_2SO_4. Found %: N 3 82, 3.78. $C_{23}H_{23}O_3N$. Calculated %: N 3.88.

We are the first to have synthesized the m-aniside of p,p-ditolylglycolic acid.

3,3-Di-(p)-tolyloxindole (p-toluisatin). (Together with N.G.Panferova.) 4.5 ml of concentrated sulfuric acid was added a little at a time with shaking, to a solution of 0.4 g of the anilide in 5 ml of glacial acetic acid. Adding the sulfuric acid turned the solution crimson, the color vanishing completely when the solution was allowed to stand for a short time. This yielded 0.38 g, or about 100% of the theoretical yield. It crystallized from alcohol as needles with a m.p. of 200-201°.

0.1580 g substance: 10 ml 0.05 N H_2SO_4; 0.1500 g substance: 9.8 ml 0.05 N H_2SO_4. Found %: N 4.43, 4.58. $C_{22}H_{19}ON$. Calculated %: N 4.44.

A sample of the substance mixed with a 3 3-di-(p)-tolyloxindole prepared by condensing isatin and toluene in the presence of concentrated sulfuric acid [1] fused without any depression of the melting point.

3,3-Di-(p)-tolyl-5-methyloxindole. Initial substances: 2.75 g of the p-toluidine of p,p-ditolylglycolic acid, dissolved in 20 ml of acetic acid, and 10 ml of concentrated sulfuric acid. The yield was 2.6 g, or about 100%.

The substance was insoluble in water, but freely soluble in most organic solvents. It crystallized from alcohol as a finely crystalline powder with a m.p. of 201°.

0.2904 g substance: 8.78 ml 0.1 N H_2SO_4. Found %: N 4.23. $C_{23}H_{21}ON$. Calculated: % N 4.0.

3,3-Di-(p)-tolyl-5-methyloxindole is not described in the literature.

3,3-Di-(p)-tolyl-7-methoxyoxindole 15 ml of concentrated sulfuric acid was added to a suspension of 3 g of the finely pulverized o-aniside of p,p-ditolylglycolic acid in 10 ml of acetic acid. We heated the contents of the flask to

40° to accelerate the reaction. The yield was 2.8 g, or close to 100% of the theoretical yield. The product obtained dissolves easily in dichlorethane and chloroform, and with difficulty in acetic acid, benzene and toluene. It crystallizes from acetic acid in colorless plates melting at 225°.

0.2234 g substance: 6.8 ml 0.1 N H_2SO_4. Found %: N 4.26. $C_{23}H_{21}O_2N$. Calculated %: N 4.08.

3,3-Di-(p)-tolyl-7-methoxyoxindole is not described in the literature.

3,3-Di-(p)-tolyl-5-ethoxyoxindole. Initial substances: 1 g of the p-phenetide of p,p-ditolylglycolic acid, dissolved in 7 ml of acetic acid, and 10 ml of concentrated sulfuric acid. The yield was 0.9 g of an air-dry product or 94.8% of the theoretical yield.

The substance was insoluble in water, alcohol, and gasoline, slightly soluble in cold acetic acid, and readily soluble in hot acetic acid. It dissolved freely in benzene, toluene, dichloroethane, and chloroform. It crystallized from glacial acetic acid as a finely crystalline powder (microscopic rhombohedra) with a m.p. of 263°.

0.1506 g substance: 4.2 ml 0.1 N H_2SO_4. Found %: N 3.90. $C_{24}H_{23}O_2N$ Calculated %: N 3.97.

3,3-Di-(p)- tolyl-5-ethyoxyoxindole is not described in the literature.

3,3-Di-(p)-tolyl-5-bromoxindole. 1 g of the p-bromanilide of p,p-ditolylglycolic acid was dissolved in 10 ml of acetic acid, and 10 ml of concentrated sulfuric acid was added. This yielded 0.93 g, or about 100% of the theoretical yield. The substance was refined by crystallizing it from alcohol - colorless rhombohedra with a m.p. of 235°.

0.1233 g substance: 0.0583 g AgBr. Found %: Br 20.11. $C_{22}H_{18}ONBr$. Calculated %: Br 20.34.

A sample mixed with the 3,3-di-(p)-tolyl-5-bromoxindole [2] prepared by condensing 5-bromisatin [4] with toluene in the presence of concentrated sulfuric acid fused without any depression of the melting point.

3,3-(p)-Tolyl-6,7-benzoxindole. (3,3-Di-(p)-tolyl-α-naphthoxindole.) Initial substances: a solution of 1 g of the α-naphthalide of p,p-ditolylglycolic acid in 20 ml of acetic acid, and 14 ml of concentrated sulfuric acid. This yielded 0.94 g, or nearly 100% of the theoretical yield.

The synthesized compound was insoluble in water, slightly soluble in ether and toluene, and freely soluble in the other organic solvents. Crystallization from a small quantity of benzene yielded a finely crystalline powder with a m.p. of 220°.

0 1526 g substance: 3.85 ml 0.1 N H_2SO_4; 0 2135 g substance. 5.6 ml 0.1 N H_2SO_4. Found : %: N 3.55, 3.67. $C_{28}H_{21}ON$. Calculated %: N 3.85.

3,3-Di-(p)-tolyl-α-naphthoxindole is not described in the literature.

3,3-Di-(p)-tolyl-4,5-benzoxindole. 3,3-Di-(p)-tolyl-β-naphthoxindole was synthesized by adding 13 ml of concentrated sulfuric acid and 1.5 g of the β-naphthalide of p,p-ditolylglycolic acid in 25 ml of acetic acid. This yielded 1.35 g, or 96.4% of the theoretical yield.

The product was insoluble in water, slightly soluble in chloroform, carbon tetrachloride, and petroleum ether, and freely soluble in the other organic solvents. It crystallized from benzene as colorless prisms. The substance grew moist at 161°, then hardened as heating is continued, and finally melted at 246.5°.

Determination of the crystallization benzene. 0.1460 g substance: 0.0200 g

C_6H_6. Found %: C_6H_6 13.7. $4C_{26}H_{21}NO \cdot 3C_6H_6$. Calculated %: C_6H_6 13.88.

Part of the substance was dried at 170-190° to constant weight and then analyzed for nitrogen.

0.2080 g substance: 5.25 ml 0.1 N H_2SO_4; 0.2596 g substance: 6.8 ml 0.1 N H_2SO_4. Found %: N 3.53, 3.66. $C_{26}H_{21}ON$. Calculated %: N 3.85.

3,3-Di-(p)-tolyl-β-naphthoxindole is not described in the literature.

SUMMARY

1. A method has been developed for synthesizing p-toluisatin and its derivatives, and a number of compounds not described in the literature have been synthesized.

2. Several aryl amides of p-p-ditolylglycolic acid have been snythesized and their properties investigated.

3. A study has been made of the influence of the nature of the radicals attached to the nitrogen atom and the carbinol carbon atom upon the intramolecular condensation rate.

4. A study has been made of the optimum quantity of sulfuric acid required for condensation as a function of the reaction temperature and the structure of the aryl amides of the α hydroxy carboxylic acids.

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Received December 19, 1949.

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SYNTHESES EMPLOYING ACRYLONITRILE

XIV. SYNTHESIS OF SUCCINONITRILE

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Succinonitrile (ethylene cyanide) is of practical interest, since succinic acid, which is widely employed in organic synthesis, is usually prepared by saponifying this nitrile. Reducing ethylene cyanide [1] yields tetramethylenediamine (putrescine), which is claimed in several patents as the starting substance for the production of synthetic polyamide fiber [2] or can be employed in synthesizing numerous compounds of high physiological activity, such as spermin [3]. Moreover, ethylene cyanide may serve as the raw material for the synthesis of vitamin B_1 [4]. The principal method of producing ethylene cyanide is reacting ethylene bromide with potassium cyanide in a water-alcohol medium. This reaction is very slow, requiring prolonged heating (30 to 40 hours), and the yields are usually low, while a large quantity of the comparatively expensive bromine is consumed. There is an assertion in the patent literature that ethylene cyanide may be synthesized by reacting acrylonitrile with hydrocyanic acid in the presence of alkali catalysts [5], but all of these methods employ the highly toxic anhydrous hydrocyanic acid, which is extremely undesirable in laboratory practice. The patent literature indicates that succinimide is produced when water is present [6].

In one of the preceeding papers in this series, A.P. Terentyev and E.V. Vinogradova have described [7] a method for adding hydrocyanic acid to ethylene oxide, which employs a solution of a mixture of potassium cyanide and magnesium sulfate instead of the anhydrous hydrocyanic acid. We have applied this method of introducing prussic acid to acrylonitrile and secured results that were satisfactory. The reaction is rapid at a low temperature (0-30°), the yields of the pure ethylene cyanide being as high as 85% [8].

In our experiments we employed pure magnesium sulfate, the reagent put out by the Chemical Board. The acrylonitrile was prepared by dehydrating ethylene cyanhydrin by the Terentyev and Vinogradova method [7], or else we used commercial (industrial) acrylonitrile, which was distilled (b.p. 76-78°) before use. Commercial potassium cyanide was used, containing about 85% KCN. Poorer grades of potassium cyanide require an increase in the quantity of magnesium sulfate employed. Thus 150 g of $MgSO_4 \cdot 7H_2O$ and 80 g of 95% potassium cyanide per mol (53 g) of acrylonitrile were required to secure good yields of ethylene cyanide. When only 90% potassium cyanide was used, correspondingly more of it had to be used, but then the quantity of magnesium sulfate used had to be increased to 370 g.

EXPERIMENTAL

A solution of magnesium sulfate saturated at room temperature (150 g $MgSO_4 \cdot 7H_2O$ in 250 ml water) was poured into a thick-walled beaker or a stock bottle. The outside of the vessel was chilled with ice, and a concentrated solution of 95% potassium cyanide (80 g in 95 g of water) was slowly added in the course of 10-15 minutes with constant chilling and stirring. Then 53 g (1 mol) of acrylonitrile was slowly added drop by drop, in the course of 2 hours, with vigorous stirring and chilling to 0-5°. The acrylonitrile dissolved as it was added, the yellowish precipitate of ethylene cyanide (succinonitrile) being thrown down at once. When all the acrylonitrile had

been added, the mixture was stirred for 3 hours at 20-30°, and the bottle was tightly sealed and allowed to stand at room temperature overnight. Then the mixture was cautiously neutralized with 50% sulfuric acid (suction draft!), with constant stirring and external chilling with ice, until its reaction was faintly acid with Congo red. The precipitate was filtered out and extracted with butyl acetate four times, both the filtrate and the precipitate being extracted. The combined extracts (totaling 350-400 ml) were washed with 30 ml of water, 30 ml of a 5% soda solution, and again with 30 ml of water. Then they were desiccated with calcium chloride and distilled in vacuum with a dephlegmator. The first to pass over was the butyl acetate, followed by the succinonitrile, which solidified in the condenser as a light-yellow mass. The residue consisted of a minute quantity of red tar. This yielded 64-68 g of succinonitrile, i.e., 80-85% of the theoretical. Redistillation in vacuum yielded the absolutely pure substance. B.p. 155-156° at 17 mm; m.p. 53°, which is in accordance with the figures given in the literature. Isoamyl acetate or ethyl acetate may be employed in the extraction, but when the latter solvent is employed it must first be washed and dried with calcium chloride to eliminate any alcohol, since otherwise it will be difficult to get rid of the traces of inorganic salts, which interfere with vacuum distillation.

The acidulation with sulfuric acid may be done after the extraction, but the operation is indispensable, since traces of alkali may produce a regeneration of prussic acid during distillation.

SUMMARY

1. A method is described for the synthesis of succinic acid (with yields of 80-85%) by reacting acrylonitrile with a saturated aqueous solution of a mixture of potassium cyanide and magnesium sulfate.

2. The example of acrylonitrile has been used to demonstrate that prussic acid can be replaced in many instances by the more convenient mixture of solutions of potassium cyanide and magnesium sulfate.

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Received December 28, 1949.

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SYNTHESIS OF ESTERS OF PHOSPHINIC ACIDS THAT CONTAIN HETEROCYCLIC RADICALS

I. SYNTHESIS OF ESTERS OF PHOSPHINIC ACIDS CONTAINING A THIAZOLE RADICAL

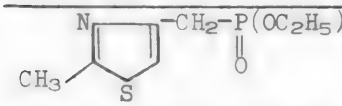
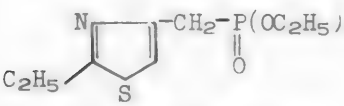
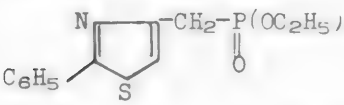
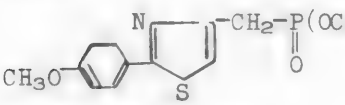
B. A. Arbuzov and B. P. Lugovkin

Very many aliphatic and aromatic phosphinic acids and their esters are known, but only very few phosphinic acids containing heterocyclic radicals. Of the phosphinic acids containing heterocyclic radicals acids with a thiophene [1], acridine [2], and pyrazole ring [3] have been synthesized.

We embarked upon the synthesis of phosphinic acids and their esters with all sorts of heterocyclic radicals. The present report sets forth the results of our synthesis of esters of some phosphinic acids that contain the thiazole ring. The initial substances we used were substitution derivatives of chloromethylthiazole and triethyl phosphite. When the constituents were heated together, an ester of a substituted thiazolylmethylphosphinic acid resulted, in accordance with the reaction pattern proposed by A.E.Arbuzov.

The ethyl esters of the thiazolylmethylphosphinic acids listed in Table 1 were synthesized in this manner.

TABLE 1

Esters of phosphinic acid	B.p.°	Pressure	d_{20}^{20}	n_D^{20}	Per cent yield
	147–150°	3 mm	1.1892	1.5030	68.1
	148–150	3 mm	1.1655	1.5000	67.2
	200–202	2 mm	1.2153	1.5650	85.3
	230–232[1]	3 mm	-	-	73.7

[1]) M.p. 47–48°.

The ethyl esters of the thiazolylmethylphosphinic acids are colorless, viscous liquids, with the exception of the ethyl ester of p-methoxyphenylthiazolylmethylphosphinic acid. When the esters were saponified with hydrochloric acid, the hydrochlorides of the respective phosphinic acids were secured; they were water-

soluble crystalline substances.

Efforts to synthesize the ethyl ester of aminothiazolylphosphinic acid were unsuccessful.

EXPERIMENTAL

Action of 4-chloromethyl-2-methylthiazole upon triethyl phosphite. 8.2 g of 4-chloromethyl-2-methylthiazole, with a b.p. of 73-75° (5 mm), n_D^{20} 1.5440 [4], was added a drop at a time to 9.7 g of triethyl phosphite, heated to 150-155°.[1] It took 30 minutes to complete the addition. After all the chloride had been added, heating was continued for an hour at 160-170°, after which the reaction product was distilled in vacuum. This yielded 9.5 g (68.1% of the theoretical) of a colorless, oily liquid with a b.p. of 147-150° (3 mm); d_{20}^{20} 1.1892; n_D^{20} 1.5030. Re-distillation caused no changes in these constants.

Analysis[2]. 0.0564 g substance: 11.76 ml NaOH (T = 0.02084)[3] Found %: P 12.03 $C_9H_{16}O_3NSP$. Calculated %: P 12.45.

Saponifying the ester. 1.8 g of the ester was heated for 6 hours to 110-125° in a sealed tube with (1:1) dilute hydrochloric acid. The resultant dark-violet solution was then heated with activated charcoal. The filtrate was repeatedly evaporated over a water bath constantly adding water, until all the hydrochloric acid had been driven off. The final evaporation left 2.1 g of the crude crystalline hydrochloride. After the substance had been recrystallized from hot water and dried at 100-115°, it began to fuse at 142°, solidifying again at 162°, and finally fusing at 167°. The per cent chlorine was found to be 11.5%, as against 15.45% called for theoretically.

Action of 4-chloromethyl-2-ethylthiazole on triethyl phosphite. 4-Choromethyl-2-ethylthiazole (4.9 g), with a b.p. of 78-80° (5 mm), n_D^{20} 1.5375, was added in the course of 30 minutes to 5.2 g of triethyl phosphite heated to 140-150°. Heating was continued for one hour at 170-180°. Vacuum distillation yielded 4.2 g (67.2% of the theoretical) of the ethyl ester of 4-phosphonomethyl--2-ethylthiazole as a colorless oily liquid with the following constants:

B.p. 148-150° (3 mm); d_{20}^{20} 1.1655; n_D^{20} 1.5000.

0.0724 g substance: 14.54 ml NaOH. Found %: P 11.58. $C_{10}H_{18}O_3NSP$. Calculated %: P 11.78.

Saponification. 2.1 g of the substance was heated with 20 ml of (1:1) hydrochloric acid for 6 hours in a sealed tube at 100-125°. Appropriate treatment (see the preceding experiment) yielded 2.1 g of the crystalline hydrochloride. The substance had an unsharp melting point of 130-135° after recrystallization from water and drying at 110-130°.

0.0910 g substance: 0.0485 g AgCl (Carius). Found %: Cl 13.18. $C_8H_{10}O_3NSP \cdot HCl$. Calculated %: Cl 14.56.

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1) Temperatures were measured within the reaction liquid in all the tests.

2) A Neumann determination of phosphorus requires prolonged heating with repeated addition of nitric acid (for as long as 30 days) in the case of compounds containing a thiazole ring. Best results are obtained when a sample is heated with concentrated nitric acid in sealed ampoules to 200-300° for 3-4 days. The difficulty of oxidizing the substances is evidently responsible for the excessively low figures for phosphorus secured during analysis.

3) The titer of the NaOH was the same in all subsequent analyses.

Action of 4-chloromethyl-2-phenylthiazole on triethyl phosphite. A mixture of 2.3 g of triethyl phosphite and 2.3 g of 4-chloromethyl-2-phenylthiazole (b.p. 140-142° at 2 mm, m.p. 40-41° [4]) was heated to 140-155° for 30 minutes and to 170-180° for one hour. Distillation yielded 2.9 g (85.3% of the theoretical) of the ethyl ester of 4-phosphonomethyl-2-phenylthiazole as a viscous liquid with the following constants:

B.p. 210-211° (5 mm); 200-202° (2mm): d_{20}^{20} 1.2153; n_D^{20} 1.5650.

0.0904 g substance: 14.66 ml NaOH. Found %: P 9.36. $C_{14}H_{18}O_3NSP$. Calculated %: P 9.96.

Saponification. 0.8 g of the substance was heated with 10 ml of 1:1 hydrochloric acid in a sealed tube for 6 hours at 110-125°. Appropriate processing yielded 0.8 g of the crystalline 4-phosphonomethyl-2-phenylthiazole hydrochloride, which had a m.p. of 180-181° after recrystallization from water and drying.

0.0684 g substance: 12.00 ml NaOH. Found %: P 10.12. $C_{10}H_{10}O_3NSP \cdot HCl$. Calculated %: P 10.63.

Action of 4-chloromethyl-2-p-methoxyphenylthiazole on triethyl phosphite. A mixture of 3 g of triethyl phosphite and 3.5 g of 4-chloromethyl-2-p-methoxyphenylthiazole (b.p. 173-176° at 3 mm; m.p. 45-46° [4]) was heated to 145-155° for 30 minutes and 170-180° for an hour and a half. The ethyl ester of 4--phosphonomethyl-2-p-methoxyphenylthiazole was an extremely viscous liquid with a b.p. of 230-232° (3 mm), which slowly crystallized. The melting point was 47-48° after recrystallization from anhydrous ether. The yield was 3.7 g, or 73.7% of the theoretical.

0.1104 g substance: 16.1 ml NaOH. Found %: P 8.41. $C_{15}H_{20}O_4NSP$. Calculated %: P 9.09.

Saponification. 1.1 g of the substance and 20 ml of 1:2 hydrochloric acid were heated together in a sealed tube for 6 hours at 110-120°. The 1.4 g of the hydrochloride was recrystallized from water (with activated charcoal) and then had a m.p. of 184-186° after drying.

0.2120 g substance: 0.0898 g AgCl. Found %: Cl 10.48. $C_{11}H_{12}O_4NSP \cdot HCl$. Calculated %: Cl 11.03.

Action of 4-chloromethyl-2-aminothiazole hydrochloride on triethyl phosphite. A mixture of 3.7 g of the hydrochloride, with a m.p. of 146° [5], and 7 g of triethyl phosphite was heated over Wood's alloy. It foamed up at 110°. The flask was heated for 1 hour at 120-140° the contents of the flask solidifying. Efforts to recover the reaction product in the pure state met with failure.

SUMMARY

1. The first representatives of esters of phosphinic acids containing a thiazole ring have been synthesized by reacting triethyl phosphite with substitution derivatives of 4-chloromethylthiazole. The ethyl esters of 2-methyl-, 2-ethyl-, 2-phenyl-, and 2-p-methoxyphenyl-4-phosphonomethylthiazoles have been synthesized.

2. Saponification of the esters of these phosphinic acids with hydrochloric acid yielded the hydrochlorides of the respective thiazolylmethylphosphinic acids.

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Received December 9, 1949.

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THE ACTION OF ACRYLONITRILE AND ACROLEIN UPON α-AND β-PYRONENES

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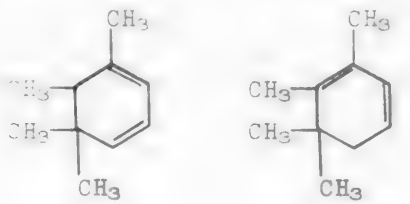
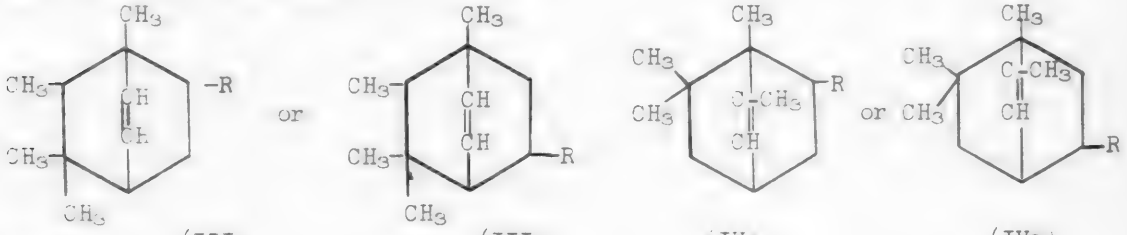
High temperatures isomerize alloocimene to the cyclic hydrocarbons α- and β-pyronene [1,2]. The pyronenes contain conjugated double bonds and can enter into a diene synthesis [3]. Their structure was established by Dupont, chiefly by investigating the addition products formed by adding the methyl ester of acetylenedicarboxylic acid and α-naphthopyrinone to them [4], and may be represented by the following formulas: Formula (I) for α-pyronene and Formula (II) for β-pyronene:



(I) (II)

In 1936 G.Dupont and R.Dulou [3] heated acrolein with fractions that were rich in β-pyronene and secured a yield of 50% of the aldehyde $C_{12}H_{19}CHO$, with the following constants: b.p. 123° (15 mm); d_0^{20} 0.973, n_D^{20} 1.4919; MR 57.24; $C_{13}H_{20}O$ F_2. Calc. 57.38. The aldehyde's semicarbazone had a m.p. of 209-210°. From the fractions that were rich in α-pyronene they secured a 10% yield of a mixture, evidently of two aldehydes which they apparently did not separate. The semicarbazone of the mixture had an unsharp melting point at 204-205°.

We repeated the experiments of G.Dupont and R.Dulou with fairly pure preparations of α and β-pyronenes, securing the corresponding addition products. The yield of the product of the addition of acrolein to α-pyronene was 40%; it was a mobile liquid with the odor of camphor and a b.p. of 98-99° (5 mm). The aldehyde's semicarbazone had a m.p. of 225°. The product of the addition of acrolein to β-pyronene was not a liquid, as Dupont and Dulou assert, but a soft paraffinlike mass. The aldehyde had a b.p. of 104-105° (3 mm). The m.p. of the aldehyde's semicarbazone was 229-230°, whereas Dupont and Dulou give the semicarbazone's m.p. as 209-210°. We did not establish the structure of the addition products of acrolein and the α- and β-pyronenes, in the sense of choosing between Formulas (III) and (IIIa) for α-pyronene and between (IV) and (IVa) for β-pyronene (R = CHO).



R = CHO (III) (IIIa) (IV) (IVa)
R = CN; NH_2 (V) (Va) (VI) (VIa)

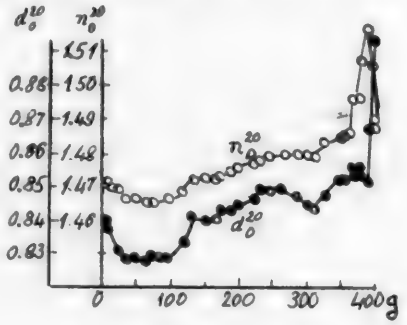
Our endeavors to synthesize the condensation product of the α- and β-pyronene aldehydes with acetone have been unsuccessful so far. We have not been able to isolate the condensation products in the pure state.

When we condensed the aldehyde of α-pyronene with acrolein in ethyl acetate with sodium present we were able to recover the condensation product as a thick liquid with a faint, pleasant odor and a b.p. of 154-157° (6 mm).

Reacting acrylonitrile with α-pyronene yielded a condensation product with a b p of 128-130° (12 mm). Acrylonitrile and β-pyronene similarly yielded a condensation product with a b.p. of 125-127° (6 mm) The compound solidified to a paraffinlike mass at room temperature which had an unsharp m.p. of 46-50°. We did not determine the structure of the addition products of acrylonitrile and β-pyronene, in the sense of choosing between Formulas (VI) and (VIa) (R=CN). Reducing the addition product of acrylonitrile and α-pyronene with sodium in alcohol yielded the corresponding amine (V) or (Va) (R = NH_3), with a b.p. of 138-140° (23 mm). Reducing the addition product of acrylonitrile and β--pyronene with sodium in alcohol yielded the amine (VI) or (VIa) (r = NH_2), with a b.p. of 125-126° (16 mm).

EXPERIMENTAL

The α- and β-pyronenes were prepared by passing alloocimene (n_D^{20} 1.5430, d_0^{20} 0.8110) at the rate of 8 - 15 drops per minute through a tube filled with broken glass at 400-420°. A total of 553 g of alloocimene was passed through. The condensate totaled 524 g and had a n_D^{19} 1.4780. Fractionationing the condensate with a column having an efficiency of 35 theoretical trays yielded 32 fractions, the constants of which are given by the following curves (see the figure). As we see from these curves the thermal isomerization of alloocimene is a complex affair, other products evidently being formed in addition to the α- and β--pyronenes. We found p-cymene and hemellitene [7] in the higher fractions of the isomerization product; this proves that the cyclization reaction is more complex than is indicated in the literature. The presence of p-cymene was proved by oxidizing it with chromic anhydride and securing the dimethyl ester of tetraphthalic acid, with a m.p. 138-139°. The hemellitene was identified by synthesizing trinitrohemellitene, with a m.p. of 205-206°.



The constants of the α-pyronene and β-pyronene fractions we isolated were close to those given by other authors, as may be seen from the following tabulation:

TABLE

α-Pyronene			β-Pyronene			
Boiling point	d_0^{20}	n_D^{20}	Boiling point	d_0^{20}	n_D^{20}	Author
30-31° (6 mm)	0.8284	1.4660	35-36° (6 mm)	0.8493	1.4795	B.A.Arbuzov and A.R. Vilchinskaya
54-56° (20 mm)	0.8272	1.4672	62-64° (20 mm)	0.8481	1.4800	Goldblatt and Palkin [1]
54-56° (20 mm)	0.8270	1.4672	62-64° (20 mm)	0.8480	1.4780	Nikitin [2]
158-159° (760)	0.8469[1]	1.4707	166-166.5°(760)	0.8437	1.4786	Rummelsburg [5]
151.5° (760 mm)	0.8280	1.4650	163.5°(760 mm)	0.8480	1.4788	Bardyshev [6]

[1] Apparently a typographical error for 0.8269.

Action of acrolein upon α-pyronene. 31.4 g of α-pyronene was heated with 14.4 g of acrolein over a water bath for 12 hours. Fractionation yielded the following fractions: 1) 6 6 g of acrolein; 2) 17.5 g up to 120° (20 mm); 3) 18.4 g at 110-114° (10 mm); 1.2 g residue. Fractionation of Fraction 3 yielded a product as a colorless liquid with the odor of camphor and the following constants:

B.p. 98-99° (5 mm); d_0^{20} 0 9764; n_D^{20} 1.4895· MR_D 56.75. $C_{13}H_{20}OF_1$. Calc. 57.38. 0.1282 g subs.: 0.3810 g CO_2; 0.1182 g H_2O. Found %: C 80.99; H 10.31. $C_{13}H_{20}O$. Calc. %: C 81.25; H 10.41.

0.2 g of the aldehyde was dissolved in 3 ml of alcohol and then poured together with 0.5 g of semicarbazide hydrochloride and 0.8 g of sodium acetate dissolved in water. The precipitated semicarbazone had a melting point of 209°. Its m.p. was 225° after recrystallization from methanol.

Action of acrolein upon β-pyronene. 20.2 g of β-pyronene was heated with 10.2 g of acrolein and a little hydroquinone over a water bath for 12 hours. Fractionation yielded the following fractions: 1) 3.2 g of acrolein; 2) 8.7 g at 63-70° (22 mm)· 3) 0.9 g up to 112° (8 mm); and 4) 14.3 g at 112-113° (8 mm). The 112-113° (8 mm) fraction soon solidified into a soft paraffin like mass. Successive tests yielded aldehyde fractions with b.p. of 104-106° (3 mm), 110-111° (7 mm), and 120° (13 mm).

0.1236 g subs.: 0.3674 g CO_2; 0.1184 g H_2O. Found %: C 81.06; H 10.72. $C_{13}H_{20}O$ Calc. %· C 81.25; H 10.41.

0.2 g of aldehyde was dissolved in 3 ml of alcohol and then poured together with 0.5 g of semicarabzide hydrochloride and 0.8 g of sodium acetate, dissolved in water. The precipitated semicarbazone had a m.p. of 229-230° after it had been recrystallized from methanol.

Condensation of the addition product of acrolein and α-pyronene with ethyl acetate. Finely cut-up sodium (6 g) was added to 153 g of ethyl acetate, the mixture was chilled to 0°, and 23.8 g of the aldehyde was gradually added in the course of an hour. The temperature within the liquid ranged from 0° to +7°. After all the aldehyde had been poured in, the whole was vigorously agitated for 2.5 hours. Then 28 ml of concentrated acetic acid was added, and the mixture was gradually diluted with 100 ml of water. The ethyl acetate layer was removed and the aqueous layer was extracted with ether the extract being washed with 6.0 N hydrochloric acid and desiccated with sodium sulfate. Driving off the solvent and distilling yielded 26.8 g of a 150-165° (6 mm) fraction. The product was secured as a thick liquid with a faint pleasant odor when this fraction was fractionated:

B.p. 154-157° (6 mm); d_0^{20} 0.9864; n_D^{20} 1.4935; MR_D 77.01; $C_{16}H_{26}O_2F_2$. Calc. 77.03. 0.1272 g subs.: 0.3636 g CO_2; 0.1094 g H_2O. Found %: C 77.96; H 9.62. $C_{16}H_{26}O_2$. Calc. %: C 77.86; H 9.92.

Action of acrylonitrile upon α-pyronene. 25.5 g of α-pyronene was heated for 20 hours to 125-140° in a sealed tube with 26 g of acrylonitrile and a small amount of hydroquinone. Fractionation of the product yielded the following fractions: 1) acrylonitrile; 2) α-pyronene at 35-46° (10 mm); and 3) 16.2 g at 120-126° (10 mm).

Distillation of Fraction 3 yielded 12.8 g of the product:

B.p. 128-130° (10 mm); d_0^{20} 0.9574; n_D^{20} 1.4875: MR_D 56.77; $C_{13}H_{19}NF_2$. Calc. 57.14. 0.1262 g subs.: 0.3810 g CO_2; 0.1174 g H_2O. 0.1148 g subs.: 7.9 ml N_2 (20°, 759 mm). Found %: C 82.33; H 10.41; N 7.81. $C_{13}H_{19}N$. Calc. %: C 82.54; H 10.05; N 7.40.

Action of acrylonitrile upon β-pyronene. 20 g of β-pyronene was heated for 20 hours to 125-140° in a sealed tube with 20 g of the nitrile and a little hydroquinone After the excess acrylonitrile had been driven off, we secured 21.5 g of a product with a b.p. of 125-127° (6 mm), which soon solidified into a paraffinlike mass that melted in the 45-50° range.

0.1136 g subs.: 0.3420 g CO_2. 0.1012 g H_2O. 0.1400 g subs.: 9.6 ml N_2 (20°, 759 mm). Found %: C 82.11; H 9.98; N 7.78. $C_{13}H_{19}N$. Calc. %: C 82.54; H 10.05; N 7.40.

Reduction of the product of the reaction between α-pyronene and acrylonitrile. 6.2 g of metallic sodium was gradually added to a solution of 6.5 g of the reaction product in 50 ml of absolute alcohol. After the reaction was over the whole was diluted with water and the aqueous solution was extracted with ether. The ether was driven off from the ether extract yielding 5.2 g of the amine – a liquid with the odor of ammonia:

B.p 138-140° (23 mm); d_0^{20} 0.9450; n_D^{20} 1.4995; MR_D 59.98. $C_{13}H_{23}NF_2$. Calc. 60.79. 0.1362 g subs.: 9.0 ml N_2 (19°, 759 mm). Found %: N 7.54. $C_{13}H_{23}N$. Calc. %: N 7.25.

0.2 g of the amine and 0.4 g of picric acid were dissolved in 7 ml of alcohol, and two hours after their solutions had been mixed, the whole was precipitated with water yielding a yellow picrate which had a m.p. of 187-188° after two recrystallizations from dilute alcohol.

Reduction of the product of the reaction between β-pyronene and acrylonitrile. This reduction was similar to the one described above. 8.4 g of the nitrile in 65 ml of absolute alcohol yielded 8.3 g of the amine, with the following constants:

B.p. 125-126° (16 mm); d_0^{20} 0.9470; n_D^{20} 1.5010; MR_D 60.09; Calc. 60.79. 0.1212 g subs.: 7.8 ml N_2 (19° 759 mm). Found %: N 7.35. $C_{13}H_{23}N$. Calc. %: N 7.25.

The amine was a rather thick liquid with an ammonia odor. The picrate was prepared as in the foregoing experiment with the α-pyronene. Its m.p. was 199-201° after recrystallization from dilute alcohol.

SUMMARY

1 The products of the diene synthesis of α- and β-pyronene with acrolein and acrylonitrile have been synthesized.

2 Reducing the products of the addition of acrylonitrile to the α- and β-pyronenes yielded the respective primary amines.

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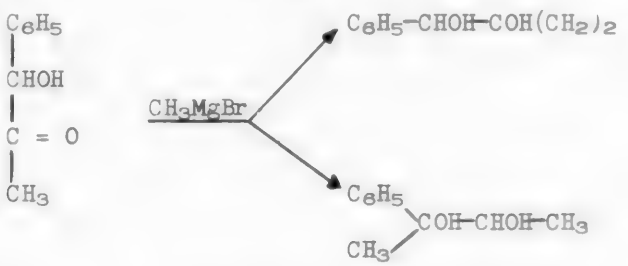
Received December 9, 1949.

RESEARCH ON THE MOLECULAR REARRANGEMENTS OF α-KETOLS

IX. REACTIONS OF METHYL-p-TOLYL KETOLS WITH ORGANOMAGNESIUM COMPOUNDS

T. I. Temnikova and L. A. Petrova

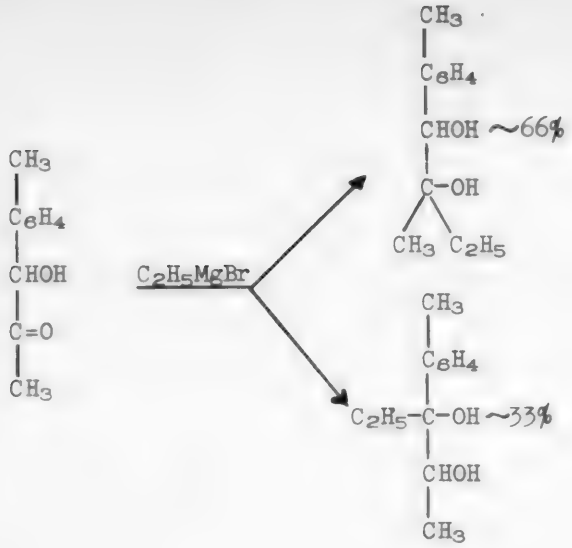
The papers by A. E. Favorsky and T. I. Temnikova [1, 2, 3] have shown that the action of organomagnesium compounds upon methyl phenyl and ethyl phenyl ketols results in the formation of glycols that are isomers of the α-ketols, in addition to the normal reaction products: the glycols that correspond to the initial compounds. This was most pronounced in the reaction of methylmagnesium bromide with phenylacetylcarbinol, a yield of some 30% of the theoretical being secured of an isomeric glycol that was an anomalous reaction product.

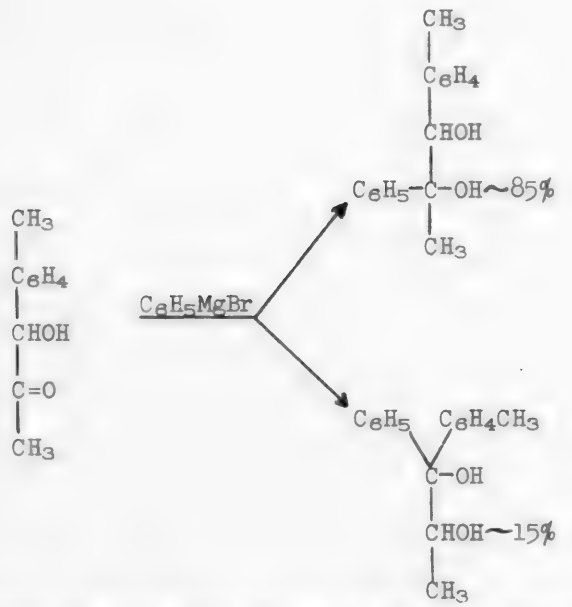


The formation of the isomeric glycol was explained on the supposition that in a transitional stage, the hydrogen atom in the carbinol group is shifted, together with an electron pair, to the positively charged carbon atom of the C = O group in the organomagnesium coordination compound [2].

We were interested in attempting to confirm the proposed rearrangement and to learn the reasons for this phenomenon. We therefore undertook an investigation of the reactions between various organomagnesium compounds and the isomeric methyl p-tolyl ketols. Introducing a methyl group at the para position of the phenyl ring guarantees an increase of the electron density in the reaction zone (the zone of the CO–CHOH group) over that prevailing in unsubstituted methyl phenyl ketols, thus causing a relative acceleration of all those processes that are promoted by the supply of electrons to the reaction zone in the intermediate coordination compound. If the diagram proposed earlier is correct, we may then expect that the rearrangement within the organomagnesium coordination compound will take place with great ease inasmuch as the transfer of a hydrogen atom, together with an electron pair, to the adjacent carbon atom has been facilitated.

Our investigation of the reaction of p-tolylacetylcarbinol with organomagnesium compounds has shown that anomalous reaction products – isomeric glycols – are actually formed, whether C_2H_5MgBr or C_6H_5MgBr is employed, in contrast to what happens with phenylacetylcarbinol.





It is worthy of note that when C_6H_5MgBr was reacted with phenylacetylcarbinol, only a single glycol was secured, the normal reaction product.

Methyl-p-toluylcarbinol ($CH_3C_6H_4-CO-CHOH-CH_3$) yielded glycols that possessed the structure of the initial ketol, 2-p-tolylbutanediol-2,3

$CH_3C_6H_4-\underset{\displaystyle CH_3}{\underset{|}{C}}OH-CHOH-CH_3$ being secured when methylmagnesium bromide was used, and 1-phenyl-1-tolylpropanediol-1,2

$$CH_3-C_6H_4\diagdown\!\!\diagup COH-CHOH-CH_3$$
$$C_6H_5$$

being secured when phenylmagnesium bromide was used.

The structure of the synthesized glycols was established as before, by

means of their oxidation products, which also serve to indicate the presence of a glycol mixture. It should be noticed that the glycol yields we secured were extremely low, and that it was very difficult to isolate them from the mixture of reaction products. In the second case, i.e., when the organomagnesium compounds were reacted with the toluyl isomer, a mixture of glycols should have been produced [4], but we were unable to prove that a glycol mixture was present.

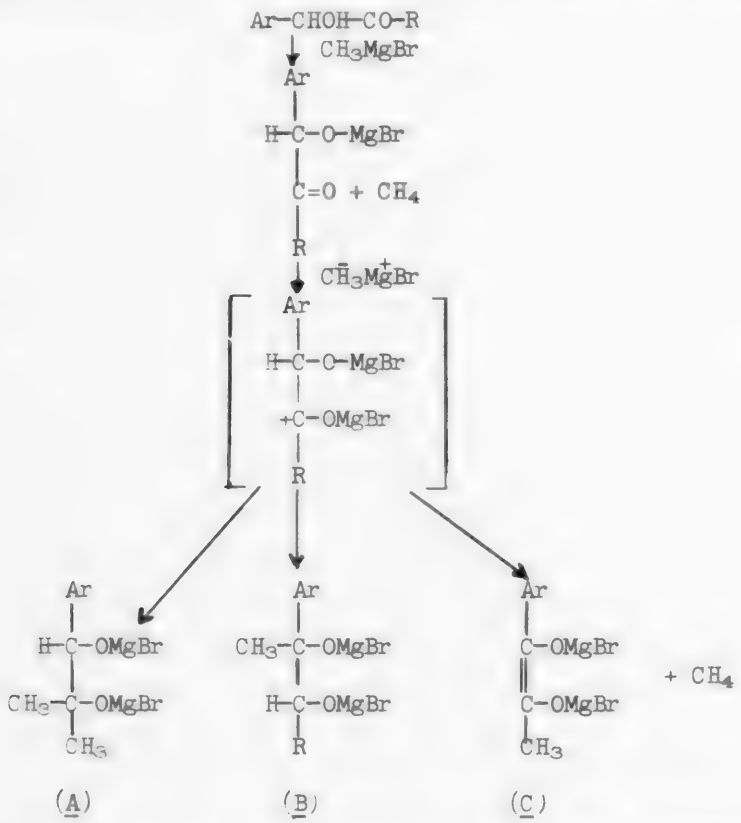
The extremely low glycol yields (18-40% of the theoretical) indicated that the normal course of the reactions of the ketols with organomagnesium compounds was paralleled by processes that lowered the principal reaction yield; processes of this sort might be the ene-diolization of the ketol by the organomagnesium compounds so that decomposition of the coordination compound with water yielded a mixture of the glycol and the ketol. This hypothesis was tested for both ketols by determining the amount of active hydrogen in reactions with methylmagnesium iodide, using the Terentyev and Shcherbakova apparatus. The results were:

1.56-1.58 for $CH_3C_6H_4$-CO-CHOH-CH_3, and
no less than 1.34-1.4 for $CH_3C_6H_4$-CHOH-CO-CH_3.

The increase in the amount of active hydrogen over the expected value (1.00) and over the figures obtained in homologs that were not ring-substituted [1]: 1.07 for C_6H_5-CO-CHOH-CH_3 and 0.94 for C_6H_5-CHOH-CO-CH_3, also indicates the peculiar influence exerted upon the properties of α-ketols by a CH_3 group in the para position of the phenyl ring. It should be borne in mind that the figures of 1.34-1.40 for the active hydrogen in the p-tolylacetylcarbinol are no doubt too low, since this ketol is usually prepared in a mixture with dimerization products that contain no atoms of active hydrogen [4].

Methyl p-tolyl ketols are not enolized in the free state since neither of the isomeric ketols colors a solution of $FeCl_3$. There is no doubt that the ketols are ene-diolized when they are reacted with organomagnesium compounds. Similar observations have been made by Kohler and Thompson in the reaction of methylmagnesium iodide with benzhydryl mesityl ketol [5] and by Weinstock and Fuson in the reactions of the phenyl mesityl ketols [6]. We know that benzoin, a compound that does not contain a CH_3 group attached to the ring, reacts normally with organomagnesium compounds, yielding glycols. The ene-diolization that occurs when organomagnesium compounds are reacted with aliphatic-aromatic ketols and benzoins that do have CH_3 groups attached to the phenyl ring is evidence of the the influence of these groups in facilitating the ene-diol rearrangement. These facts likewise enable us to clear up the mechanism involved in the reaction of ketones and ketols with organomagnesium compounds. We know from research on the kinetics of bromination and hence the ene-diolization of ring-substituted acetophenones that the velocity constant of ene-diolization falls when electron donor substituents are introduced into the ring in an alkaline medium, rising when the same substituents are introduced into the ring in an acid medium [7]. As has been shown by other authors and by us, the ene-diolization of ketols when they are reacted with organomagnesium compounds is facilitated when a methyl group, which is an electron donor group, is introduced into the phenyl ring. It follows from these observations that the reaction of organomagnesium compounds with ketones is like the mechanism of catalysis during the enolization of carbonyl compounds in an acid medium, i.e., it begins by attacking the oxygen atom of the carbonyl group. Then the negatively charged hydrocarbon group in the organomagnesium compound is either added to a carbon atom, yielding a normal addition product,

or else is combined with a hydrogen atom, split out as a proton, the reaction thus yielding a magnesium-bromine enolate; the negatively charged group in the organomagnesium compound apparently acts merely as a proton acceptor therein, facilitating the splitting out of the proton from the carbonyl compound. The more advantageous the formation of the double bond in the respective magnesium-bromine enolate, from the standpoint of the energy involved and the harder it is for the normal addition reaction to take place, the more will the reaction of ketones and ketols with organomagnesium compounds tend toward enolization. The enolization process resembles the processes of splitting out water from alcohols and hydrahalic acids from halogenated derivatives – in an acid medium – processes that chiefly involve the splitting out of hydrogen from the least hydrogenated carbon atom, in accordance with the Zaitsev rule, i.e., the splitting out of the least protonized hydrogen. The entire reaction of organomagnesium compounds with α-ketols may be represented as follows:



As a rule, α-ketols react only to form α-glycols (A); aliphatic-aromatic α-ketols, containing R = CH_3 and C_2H_5, have manifested an ability to react anomalously, yielding isomeric glycols (B); and, lastly, in Ar–$CH_3C_6H_4$ compounds, the influence of the CH_3 group in the para position of the phenyl ring upon the CHOH–CO group gives rise to still another reaction course, yielding a magnesium ene-diolate (C).

EXPERIMENTAL

I. Reaction of Methyl-p-toluylcarbinol With Organomagnesium Compounds

Methyl-p-toluylcarbinol was prepared by the Klinge method, from α-bromoethyl p-tolyl ketone, the resulting preparation containing about 20% of the isomeric ketol [4].

Determination of active hydrogen in reaction with CH_3MgBr (Terentyev-Shcherbakova method):

0.1494 g subs.: 35.59 ml CH_4 (10.9°, 728 mm); 0.0686 g subs.: 15.5 ml. CH_4 (17.1°, 772.7 mm). Found: active H 1.58, 1.54.

Action of CH_3MgBr on the ketol. 4.9 g of methyl-p-toluylcarbinol in ether was added to an ether solution of CH_3MgBr, prepared from 2.9 g of Mg and 11.6 g of CH_3Br, chilled with ice. The reaction was very energetic. The reaction mixture was allowed to stand for 12 hours, and then was heated for 4 hours. After it had cooled, it was decomposed with water. The ether extract was dried with $MgSO_4$. The ether was driven off, and the residual oil was distilled in vacuum, the bulk distilling at 160-163° at 10 mm and crystallizing within 3 days. M.p. 54-56°. The yield was 2.7 g, or 49.4% of the theoretical.

0.1108 g subs.: 0.2992 g CO_2; 0.0855 g H_2O. 0.1016 g subs.: 0.2730 CO_2; 0.0816 g H_2O. Found %: C 73.64, 73.28; H 8.93, 8.98. $C_{11}H_{16}O_2$. Calc. %: C 73.33; H 8.88.

Oxidation of the glycol. 1.5 g of CrO_3 in 15 ml of H_2O was added to 2 g of the glycol and 6 g of $KHSO_4$, and the mixture was heated to 50°. The oxidation products were driven off with steam. After the oxidation products had been processed in the usual manner [1, 2], the following products were identified in them: acetaldehyde as its p-nitrophenylhydrazone, with a m.p. of 124-125° (the mixed melting point was the same), and methyl p-tolyl ketone as its semicarbazone, with a m.p. of 203-204° (a fusion sample had the same m.p.). No acetone was found among the oxidation products. The acid distillate yielded a minute quantity of p-toluic acid.

Action of phenylmagnesium bromide upon methyl-p-toluylcarbinol. An ether solution of 5 g of the ketol was added to an organomagnesium compound, prepared with 5 g of Mg and 19 g of bromobenzene. The mixture was allowed to stand for 12 hours, and then was heated for 6 hours to the ether's boiling point. After the mixture had been decomposed with water and a dilute solution of acetic acid the ether extract was washed with water and with soda. the ether then being driven off, and the residue distilled with steam to remove the diphenyl, benzene, and other volatile products. The residual oil was extracted with ether, and the ether extract washed with $MgSO_4$. The ether was driven off, and the oil crystallized after standing for 2 months. The crystals weighed 1.7 g, or a yield of 20% of the theoretical, based upon the glycol. The synthesized 1-phenyl-1-tolylpropanediol was recrystallized from petroleum ether, after which its m.p. was 84.86°.

0.0793 g subs.: 0.2292 g CO_2; 0.557 g H_2O. 0.0860 g subs.: 0.2510 g CO_2; 0 0574 g H_2O. Found %: C 78.83, 78.77; H 7.86, 7.47. $C_{16}H_{18}O_2$. Calc. %: C 79.33; H 7.44.

Oxidation of the glycol. The glycol was oxidized with lead tetraacetate [8]: 0.48 g of the glycol, 25 ml of CH_3COOH, and 4 g of freshly prepared lead tetraacetate. The oxidation yielded acetaldehyde, identified as its p-nitrophenylhydrazone, with a m.p. of 120° (a fusion sample mixed with the p-nitrophenylhydrazone of acetaldehyde exhibited no depression of the melting point), and phenyl p-tolyl ketone, with a m.p. of 51-53° (a fusion sample mixed with specially prepared phenyl p-tolyl ketone had the same m.p.).

II. Reaction Organomagnesium Compounds With p-Tolylacetylcarbinol

p-Tolylacetylcarbinol was prepared from α-bromo-α-tolylacetone by the method described previously [4].

Determination of active hydrogen in reaction with CH_3MgBr (Terentyev-Shcherbakova method):

0.0671gsubstance: 13.9 ml CH_4 (13.3°, 756.8 mm); 0.0543 g substance: 10.5 ml CH_4 (14°,755.4). Found: active H 1.40, 1.34.

Action of C_2H_5MgBr with p-tolylacetylcarbinol. 5 g of the ketol was used in this reaction, which was carried out as described above. Fractionation in vacuum yielded 1.7 g of an oil with a b.p. of 143-149° at 5 mm.

0.112 g substance: 0.3010 g CO_2; 0.0909 g H_2O; 0.1260 g substance: 0.3420 g CO_2; 0.1033 g H_2O. Found %: C 73.82, 74.02; H 9.13, 9.12. $C_{12}H_{18}O_2$. Calculated %: C 74.23; H 9.28.

Oxidation of the glycol. The glycol was oxidized, using 1.5 g of the glycol and 4 g of lead tetraacetate in 20 ml of CH_3COOH. The following products were identified after the oxidation products had been appropriately processed [1,8]: acetaldehyde as its p-nitrophenylhydrazone, with a m.p. of 119-120°, which exhibited no depression of the melting point when mixed with the known preparation; ethyl methyl ketone as its semicarbazone, with a m.p. of 140° (a fusion sample mixed with the known product, with a m.p. of 142°, had a m.p. of 140-141°); ethyl p-tolyl ketone as its semicarbazone, with a m.p. of 183-184° (the mixed melting point was the same); and p-toluic acid, with a m.p. of 172-174° (the mixed melting point was the same).

The presence of ethyl methyl ketone and ethyl p-tolyl ketone in the oxidation products is evidence of the formation of the following glycols when C_2H_5MgBr is reacted with $CH_3C_6H_4$-CHOH-$COCH_3$ 1-p-tolyl-2-methylbutanediol-1,2 and 3-p-tolylpentanediol-2.3. The yield of 0.5 g of the semicarbazone of ethyl p-tolyl ketone from 1.5 g of the glycol mixture indicates that the mixture contained at least 33% of 3-p-tolylpentanediol-2,3.

Action of phenylmagnesium bromide on p-tolylacetylcarbinol. An ether solution of 6 g of the ketol (m.p. of 105-107° at 2 mm) was added to an ether solution of phenylmagnesium bromide, prepared from 3.6 g of magnesium and 23 g of bromobenzene. The usual processing [1,2] yielded 5.1 g of an oil, which hardened within 2 months. The substance fused at 87-88° after recrystallization from ligroin and colored concentrated H_2SO_4 a bright blue. The yield was 2.6 g, or 18% of the theoretical.

0.0917gsubstance: 0 2678 g CO_2; 0.0625 g H_2O; 0.0909 g substance: 0.2642 g CO_2; 0.0641 g H_2O. Found %: C 79 64, 79.27; H 7.77, 7.88. $C_{16}H_{18}O_2$. Calculated %: C 79.33; H 7.44.

Oxidation of the glycol was done with 1 g of the substance and 4 g of lead tetraacetate. The following were identified after the usual processing of the oxidation products: acetaldehyde as its p-nitrophenylhydrazone, with a m.p. of 119-120°; phenyl p-tolyl ketone, with a m.p. of 54-55°; acetophenone as its semicarbazone, with a m.p. of 194.5-196°; and p-toluic acid, with a m.p. of 173-175°. None of these substances exhibited a depression when mixed with the known product.

A qualitative and a rough quantitative calculation of the oxidation products indicated that the substance was a mixture of the following glycols: 1-p-tolyl-2-phenylpropanediol-1,2 and 1-phenyl-1-p-tolylpropanediol-1,2 in about the proportions of 7:1.

SUMMARY

1 A study has been made of the reaction of methyl-p-toluylcarbinol and p-tolylacetylcarbinol with organomagnesium compounds, and it has been shown that they are appreciably ene-diolized (as much as 40-60%) when reacted with CH_3MgBr.

2 The reaction of methyl-p-toluylcarbinol with organomagnesium compounds produces slight yields of a glycol with the same structure as the ketol.

3. The reaction of C_2H_5MgBr with p-tolylacetylcarbinol yields the isomeric glycol 3-p-tolylpentanediol-2,3 (about 33%) in addition to the normal reaction product; the action of phenylmagnesium bromide likewise produces a small yield of an isomeric glycol: 1-phenyl-1-p-tolylpropanediol-1,2.

4 It has thus been shown that the introduction of a CH_3 group at the para position in the phenyl ring of aliphatic-aromatic α-ketols facilitates their ene-diolization when they are reacted with organomagnesium compounds and increases the yield of anomalous reaction products. These facts confirm the outline previously put forward for the reaction of ketols with organomagnesium compounds.

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Received December 29, 1949.

The A.E.Favorsky Laboratory of Organic Chemistry, The A.A. Zhdanov State University of Lenigrad, Awarded the Order of Lenin.

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[1]) See Consultants Bureau English translation, p. 745.

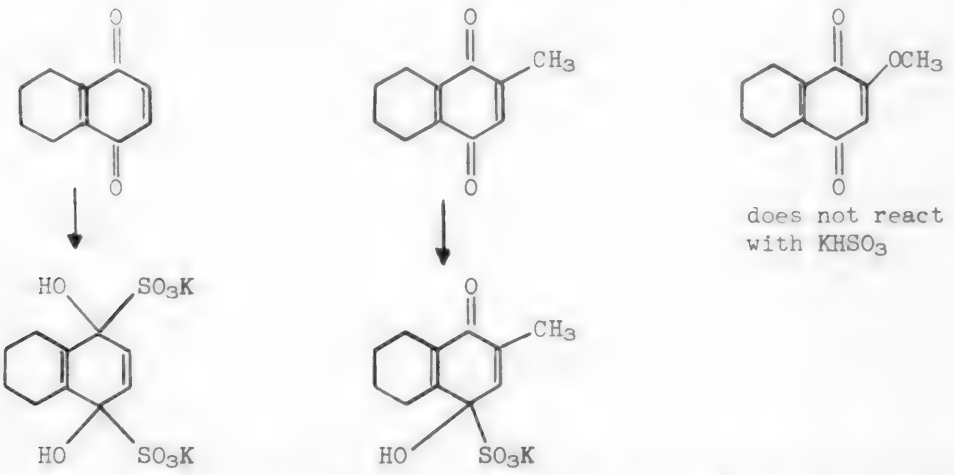
RESEARCHES ON BISULFITE COMPOUNDS

XIV. THE STRUCTURE OF THE BISULFITE COMPOUND OF 2-METHYL-1,4-NAPHTHOQUINONE AND ITS REACTION WITH PHENYLHYDRAZINE

V. N. Ufimtsev and M. I. Chernyak

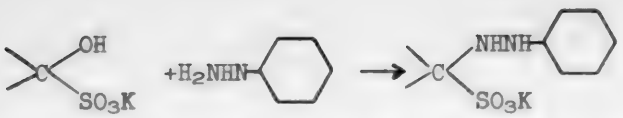
We have employed a series of compounds, especially resorcinol, 1-nitroso-2-naphthol, and 1,4-naphthoquinone [1], to show that bisulfite is added to these compounds at the oxo group of the respective quinone or the quninone form of the hydroxy compound. Jackson and Beggs secured compounds of similar structure by reacting bisulfite with derivatives of benzoquinone [2].

The following relationship may be observed in the derivatives of 1,4-naphthoquinone:

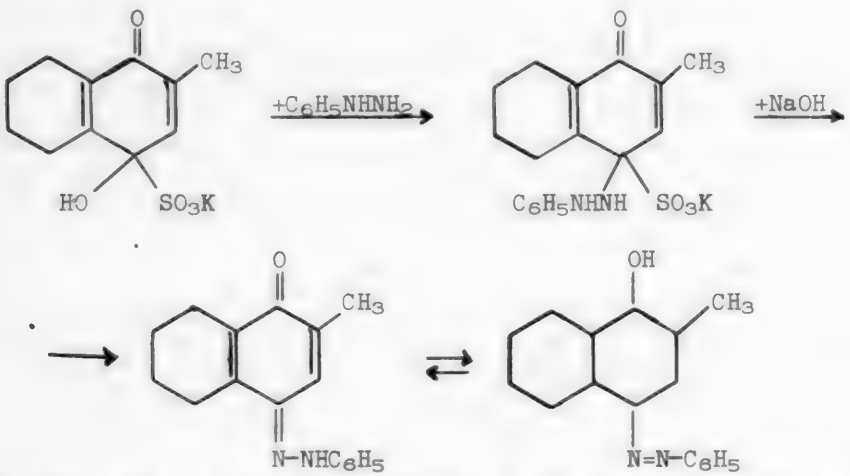


When no steric hindrance is present, both of the oxo groups in the quinone react; a methyl group prevents the adjacent oxo group from reacting [1]; and lastly, a methoxy group prevents both the adjacent ortho oxo group and the oxo group in the 4 position from reacting [3]. The last circumstance is not surprising, as analogous hindrances are reported in the paper by Chelintsev and Dubinin on their efforts to employ the bisulfite reaction for 8-hydroxy-6-methoxyquinoline [4].

In their paper on the reaction of phenylhydrazine and its derivatives with a bisulfite compound of 2-methyl-1,4-naphthoquinone, Bochvar and his co-workers cast doubt on the formula we have given for the structure of this bisulfite compound, and deduce from its reactivity with phenylhydrazine and 4-nitrophenylhydrazine that it contains an oxo group capable of these reactions [5]. In so doing, they ignore the older papers by Bucherer and his associates and subsequent authors [6], as well as our recent researches [7], which indicate that bisulfite compounds of the naphthols and their derivatives can react with hydrazines, phenylhydrazines, and their derivatives in accordance with the following general equation:



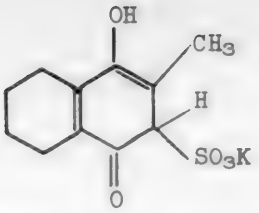
Hence the fact of a reaction with phenylhydrazine cannot serve as proof of the presence of an oxo group, this reaction of the bisulfite compound, as well as the decomposition of the resulting product by alkaline reagents, yielding 2-methyl-4-benzeneazo-1-naphthol, as is easily represented by the following diagram:



This reaction with phenylhydrazine and its derivatives is much easier with 2-methyl-1,4-naphthoquinone itself than with its bisulfite compound. When we compared the reactivity of these two compounds with 4-nitrophenylhydrazine in dilute solutions in the cold, we found that the reaction proceeds easily with 2-methyl-1,4-naphthoquinone, while no reaction is observed when parallel tests are made with its bisulfite compound. This led us to conclude that these two compounds had different structures[1].

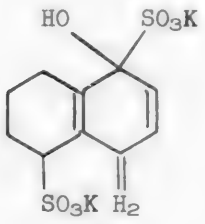
The reaction conditions were essentially different in the experiments made by Bochvar and his associates (pH of the medium, an approximately tenfold increase in the concentration of the two reagents); this may, of course, increase the reactivity of the less active compound [8]. The method employed by the authors cited to isolate the product of the reaction between the bisulfite compound of 2-methyl-1,4-naphthoquinone and phenylhydrazine was highly complicated and inaccurate; the product itself was described, without adequate grounds therefor, as a substance with abnormal colloidal properties; the analysis of the substance, which yielded excellent results, was made with an uncrystallized product. Our experiments have shown that the product of the reaction of the bisulfite compound of 2-methyl-1,4-naphthoquinone with phenylhydrazine crystallizes as its sodium salt with varying amounts of water, as so often happens: both anhydrously and with 5 molecules of crystallization water, which suffices to explain all its "abnormal" properties.

When we consider the formula proposed by Bochvar and his associates for the structure of the bisulfite compound of 2-methyl-1,4-naphthoquinone:

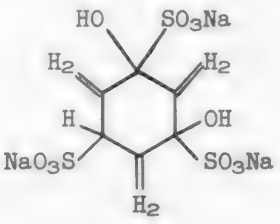


we find that it exhibits one hydroxy group, which ought to be discoverable by the usual analytical reactions (such as acylation). This hydroxy group is readily detected in 2 methyl-1,4-naphthoquinone, since heating with acetic anhydride yields 2-methyl-1,4-diacetylnaphthohydroquinone [9], so that the presence of the methyl group at the 2 position does not interfere with the acylation reaction. According to our old, unpublished experiments bisulfite compounds of the naphthols and phenols cannot be acetylated under ordinary conditions. This behavior largely reminds us of the well-known findings on the acetylation of alcohols, which likewise does not take place or does so with great difficulty in tertiary alcohols of similar structure: [10].

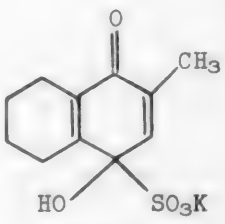
We repeated our old experiments and again found the bisulfite compounds of 1-naphthol-5-sulfonic acid (I), resorcinol (II), and 2-methyl-1,4-naphthoquinone (III) are not acetylated under ordinary conditions, the original substances being recovered with good yields after the reaction was over. Hence, the formula proposed by Bochvar and his associates for the structure of the bisulfite compound of 2-methyl-1,4-naphthoquinone is not confirmed.



(I)



(II)



(III)

EXPERIMENTAL

1. Reaction of the sodium salt of the bisulfite compound of 2-methyl-1,4-naphthoquinone with phenylhydrazine. 5 g of the sodium salt of the bisulfite compound of 2-methyl-1,4-naphthoquinone was dissolved in 10 ml of water. 2 g of phenylhydrazine was dissolved in 5 ml of glacial acetic acid and 5 ml of water. The two solutions were mixed together and set aside to stand. The next day the precipitate was filtered out, washed with 30 ml of ethyl alcohol and then with 50 ml of benzene, and dried in a desiccator. This yielded 4.5 g of brownish-orange needles. The substance was very freely soluble in water, slightly soluble in ethyl alcohol, and insoluble in ether.

a) Aqueous form. 3.9 g of the substance was quickly dissolved in the cold in 100 ml of ethyl alcohol and filtered (a reddish-brown residue being left on the filter, the insoluble substance weighing 0.6 g). The solution was chilled to 0°,

whereupon 1.3 g of brownish-orange needles was thrown down.

0.1597 g, 0.1204 g substance: 0.0245 g, 0.0184 g Na_2SO_4; 0.1051 g substance: 0.0204 g H_2O Found %: Na 4.97, 4.95; H_2O 19.41 $C_{17}H_{15}O_4N_2SNa \cdot 5H_2O$. Calculated %: Na 5.04; H_2O 19.73

b) Anhydrous form. 5 g of the substance was treated in the cold with 100 ml of ethyl alcohol, and the undissolved product was filtered out, the deposit on the filter weighing 2.4 g. 250 ml of ether was added to the filtrate, an orange precipitate settling out at first, turning into the elongated bright greenish-yellow needles of the anhydrous form upon standing; weight 1.45 g.

0.1362 g substance: 0.0266 g Na_2SO_4. Found %: Na 6.32. $C_{17}H_{15}O_4N_2SNa$ Calculated%: Na 6.28

Similar results may be obtained by carefully drying out the substance in a vacuum desiccator, treating it quickly with ethyl alcohol and filtering at once; the yellow needles of the anhydrous form settle out of the filtrate abundantly within a short time.

2. Reaction of the potassium salt of the bisulfite compound of 2-methyl-1,4-naphthoquinone with phenylhydrazine. 5 g of the potassium salt of the bisulfite compound of 2-methyl-1,4-naphthoquinone was dissolved in 12.5 ml of water. 2 g of phenylhydrazine was dissolved in 5 ml of acetic acid and 5 ml of water. The two solutions were mixed together; two days later the resultant red-orange mass was filtered out, and the precipitate well washed with ether and air-dried; it weighed 6.1 g

5.4 g of the substance was purified by processing it three times as follows: it was triturated with 5 ml of water and then with 100 ml of ethyl alcohol, after which it was filtered. The combined filtrates were chilled to 0°, throwing down yellow needles, which were filtered out, washed with alcohol and with benzene, and dried in a vacuum desiccator; the purified substance weighed 2.45 g. The substance was readily soluble in water, slightly soluble in ethyl alcohol, and insoluble in ether; it contained no crystallization water.

0.1634 g substance: 0.0374 g K_2SO_4. Found %: K 10.27. $C_{17}H_{15}O_4N_2SK$. Calculated%: K 10.22.

3. Acetylating the bisulfite compound of 1-naphthol-5-sulfonic acid. 1.5764 g of the potassium salt of the bisulfite compound of 1-naphthol-5-sulfonic acid was dissolved in 5 ml of water, 5 ml of acetic anhydride was added, and the whole was heated to a boil for an hour. The reaction mass was dried in a vacuum desiccator and weighed after the darker portion had been removed. The weight was 1.23 g. Analysis indicated that no acetylation took place.

0.1573 g substance: 0.0714 g K_2SO_4. Found %: K 20.37. $C_{10}H_8O_7S_2K_2$ Calculated %: K 20.45.

4. Acetylating the bisulfite compound of resorcinol. 10 g of the sodium salt of the bisulfite compound of resorcinol and 20 ml of acetic anhydride were heated over a water bath for 2 hours with a reflux condenser, the external appearance of the mass showing no change. Then the reaction mass was cooled, and the reaction product was filtered out, washed with ethyl alcohol, and dried in a vacuum desiccator. This yielded 9.6 g of a colorless crystalline precipitate. Analysis showed that no acetylation occurred.

0.1650 g substance: 0.0794 g Na_2SO_4. Found %: Na 15.58. $C_6H_8O_{11}S_3Na_3 \cdot H_2O$. Calculated %: Na 15.67.

5. Acetylating the bisulfite compound of 2-methyl-1,4-naphthoquinone. 4.6 g of the potassium salt of the bisulfite compound of 2-methyl-1,4-naphthoquinone and 10 ml of acetic anhydride were heated over a water bath for 2 hours with a reflux condenser. Then the reaction mass was cooled, and the precipitate filtered out and washed with ether. This yielded 4.05 g of a colorless crystalline precipitate (stubby prisms). Qualitative test: when a solution of potassium carbonate was added to an aqueous solution of the precipitate, the light-yellow needles of 2-methyl-1,4-naphthoquinone with a m.p. of 103-105°, were thrown down.

0.1562 g substance: 0.0467 g K_2SO_4. Found %: K 13.42. $C_{11}H_9O_5SK$. Calculated %: K 13.37.

The precipitate was recrystallized from dilute methanol. A repeated analysis indicated that no acetylation took place.

0.1628 g substance: 0.0484 g K_2SO_4. Found %: K 13.34.

SUMMARY

1. The reaction of the bisulfite compound of 2-methyl-1,4-naphthoquinone with phenylhydrazine is the normal reaction of this compound.

2. The bisulfite compounds of 1-naphthol-5-sulfonic acid, resorcinol, and 2-methyl-1,4-naphthoquinone are not acetylated when they are boiled with acetic anhydride, which contradicts the structure proposed by Bochvar and his associates for the last of these three compounds.

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Received December 25, 1949.

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RESEARCH ON SULFONATION

XVIII THE EQUILIBRIUM BETWEEN p-DICHLOROBENZENESULFONIC ACID AND ITS ACID CHLORIDE

A. A. Spryskov and Yu. L. Kuzmina

Earlier[1] we described the equilibrium of p-toluenesulfonic acid and its acid chloride in a medium consisting of a mixture of sulfuric and chlorosulfonic acids. Our experimental results were used to calculate the equilibrium constant, the value of which ranged from 0.9 to 1.6, depending upon the results of the individual tests. When we calculated the percentage of the acid chloride in the equilibrium mixture, using the mean value of the equilibrium constant, the results we secured differed from those secured experimentally by as much as 5% in individual experiments. We proved that the reasons for these discrepancies between the calculated values and those found experimentally are the partial hydrolysis of the chloride when the mixture was poured out over ice and the sulfonation of the sulfochloride, yielding as much as 4% of the disulfo derivative.

An effort has been made in the present research to study the equilibrium of a sulfo acid with its acid chloride, using an acid chloride that resists hydrolysis better and is not sulfonated to a disulfo derivative under the experimental conditions. We selected 1,4-dichlorobenzene-2-sulfochloride, which was prepared by reacting chlorosulfonic acid with p-dichlorobenzene in a nearly pure state at 114°. We found that no disulfochloride is formed at this temperature, which enabled us to investigate the equilibrium at various temperatures with a view to calculating the heat absorbed or evolved in the conversion of the acid chloride to a sulfo acid. The equilibria were tested from 0 to 80°.

Table 1 lists the results of the experiments in which the reaction mixture was kept at 0°. Preliminary tests showed that a state approaching equilibrium is not reached within 6-9 hours as was the case with p-toluene sulfochloride. About 20 hours are required to reach equilibrium with p-dichlorobenzene sulfochloride, provided the mixture contains a large enough percentage of chlorosulfonic acid. When the percentage of chlorosulfonic acid drops while that of the sulfuric acid rises, this time interval is insufficient for the attaining of a state approaching equilibrium, as is shown by the results of Test 62. After 22 hours have passed the percentage of the chloride continues to fall. This led us to keep some mixtures as long as 150 hours.

If m mols of sulfuric acid and n mols of chlorosulfonic acid are employed per mol of the acid chloride, the equilibrium constant is calculated from:

$$K=\frac{(x)\cdot(n+x)}{(1-x)\cdot(m-x)}.$$

after equilibrium is reached in the equation:

$$\underset{1-x}{RSO_2Cl}+\underset{m-x}{H_2SO_4}\rightleftarrows\underset{x}{RSO_3H}+\underset{n+x}{HSO_3Cl}$$

[1] Report XVI, cf J.Gen.Chem 21, 714 (1951).

TABLE 1

State of Equilibrium Between p-Dichlorobenzenesulfonic Acid and its Acid Chloride at 0°.

Test No.	Mols used per mol of the chloride		Time the mixture was kept, hours	Chloride yield, % of original	Equilibrium constant
	H_2SO_4	HSO_3Cl			
70	1.21	5.08	32	85.4	—
			48	86.7	0.74
			56	86.4	0.76
68	2.50	5.19	32	77.4	0.69
			52	78.0	0.67
55	3.43	4.11	10	72.3	—
			22	70.8	0.58
			32	71.1	0.57
54	3.77	4.18	9	73.8	—
			22	68.0	0.61
			34	67.7	0.62
62	4.17	2.77	9	77.3	—
			22	69.1	—
			32	65.4	—
63	4.41	2.83	75	58.4	0.58
			100	59.2	0.56
			150	58.3	0.58
65	6.32	2.46	150	47.1	0.58
			Average		0.63

The value of the equilibrium constant varied by a factor of 1.3 in some tests, while the ratio of the sulfuric acid to the chlorosulfonic acid varied by a factor of 13. The percentage of the acid chloride converted into the sulfo acid likewise varied within a wide range, from 15 to 53%.

The experimental equilibrium constant enables us to calculate the percentage of the sulfo acid from the equation:

$$x = \frac{n+K+Km \pm \sqrt{(n+K+Km)^2-4(K-1)Km}}{2(K-1)}.$$

Table 2 gives the percentage of the acid chloride, $1 - x$, as calculated from this equation, and the mean values observed experimentally after a state approaching equilibrium had been reached.

We see that the discrepancy between the calculated and experimentally observed percentages of the acid chloride in the equilibrium mixture did not exceed 2.2%.

Table 3 gives the results of our determination of the equilibrium constant of p-dichlorobenzenesulfonic acid and its acid chloride at 80°. The fluctuations of the values of the constant as calculated for the various runs are extremely small. The ratio of the sulfuric acid to the chlorosulfonic acid varies by a factor of more than 12 in various tests, while the percentage of the chloride converted into the sulfo acid ranges from 81 to 14%. When a state approaching equilibrium is reached at 80°. 30 minutes suffice for high percentages of chlorosulfonic acid, a somewhat longer time being required when the percentage of sulfuric acid in the mixture exceeds that of the chlorosulfonic acid.

TABLE 2

Equilibrium Between p-Dichlorobenzene-sulfonic Acid and Its Acid Chloride at 0°.

Test No.	Sulfochloride in the mixture, % of the original quantity		Per cent discrepancy
	Observed	Calc.	
70	86.6	88.2	-1.6
68	77.7	79.1	-1.4
55	71.0	69.3	+1.7
54	67.9	67.6	+0.3
63	58.8	56.6	+2.2
65	47.1	45.3	+1.8

The percentage of acid chloride in the equilibrium system $(1 - x)$, calculated from the formula cited above, and the mean values of the experimental observations after a state approaching that of equilibrium had been reached are listed in Table 4.

In these experiments, the difference between the calculated and observed values does not exceed 1.1%.

We made no attempt to calculate the heat involved in the reaction, since the extremely small difference between the values of the equilibrium constant for 0 and 80° indicated that the heat involved in the conversion of the acid chloride into the sulfo acid is either zero or negligibly small under the conditions prevailing.

TABLE 3

State of Equilibrium Between p-Dichlorobenzenesulfonic Acid and Its Acid Chloride at 80°

Test No	Mols used per mol of the chloride		Time the mixture was kept, hours	Chloride yield % of original	Equilibrium constant, K
	H_2SO_4	HSO_3Cl			
73	1.42	5.24	1	86.6	0.65
			3	86.1	0.68
			6	86.5	0.65
74	2.33	5.48	2.5	79.2	0.70
			5	80.0	0.67
75	3.17	4.20	0.5	70.4	0.66
			2.5	70.4	0.66
			5	70.3	0.66
76	4.71	3.10	3	55.3	0.67
			6	55.1	0.68
78	5.59	2.68	0.25	48.5	-
			1	47.1	0.71
			6	47.7	0.69
84	6.73	2.07	1	39.2	-
			4	38.7	0.69
			8	38.6	0.70
80	6.17	0	8	18.8	0.65
				Average	0.67

EXPERIMENTAL

100% sulfuric acid was prepared by distilling sulfuric anhydride from oleum into chemically pure sulfuric acid. Analysis indicated that it contained 100.16% H_2SO_4.

TABLE 4

Equilibrium Between p-Dichlorobenzenesulfonic Acid and Its Acid Chloride at 80°

Test No.	Sulfochloride in the mixture, % of the original quantity		Per cent discrepancy
	Observed	Calculated	
73	86.4	86.2	+0.2
74	79.6	79.9	−0.3
75	70.4	70.0	+0.4
76	55.2	55.3	−0.1
78	47.4	48.5	−1.1
84	38.7	39.4	−0.7
80	18.8	18.5	+0.3

The chlorosulfonic acid was distilled at 86-89° and a pressure of 22-35 mm. The chlorosulfonic acid used in our study of equilibrium at 0° was analyzed by titration against alkali and was found to contain 97% HSO_3Cl and 3% H_2SO_4. In the tests run at 80° we used a chlorosulfonic acid containing 95.2% HSO_3Cl and 4.8% H_2SO_4.

Sulfonation of p-dichlorobenzene with chlorosulfonic acid yielded p-dichlorobenzene sulfochloride, with a m.p. of 36.5°, recrystallization from ether yielding a product with a m.p. of 37.5–38°. The percentage of the chloride that was hydrolyzed when the reaction mixture was poured out over ice was determined by dissolving a sample of the chloride in the chlorosulfonic acid before the equilibrium test began and pouring the solution over ice, the chloride being filtered out, washed, dried in a dessiccator, and weighed. The losses sustained in three tests were 1.7, 2.1 and 2.1%, respectively, of the sample's weight. Inasmuch as the chlorosulfonic acid contained 3% sulfuric acid, we deducted the percentage of chloride converted into the sulfo acid at equilibrium, finding it to be 1.94%. To be sure, the state of equilibrium had not been reached in these tests, but the percentages nonetheless indicate that only fractions of one per cent of the chloride are lost when the mixture is poured over ice, washed and dried.

The equilibrium experiments were run as follows. Sulfuric acid, chlorosulfonic acid, and the chloride were successively added to a container, each reagent being weighed after it had been added, the chloride dissolving readily in the acid mixture. The mixture was kept in thawing ice or in an Eickmann apparatus, with ethyl alcohol and water boiling in the latter's outer container. The temperature within the Eickmann apparatus was held within 80 ± 0.2°. Samples were taken of the mixture at the stipulated intervals of time, weighed and poured over ice The melting point of the chloride recovered from the equilibrium mixture was determined nearly always. It never fell below 36-37°, being 37-38° in most cases, i.e., it did not change during the run.

In calculating the constant we applied the appropriate correction for the percentage of sulfuric acid in the chlorosulfonic acid.

SUMMARY

A study has been made of the equilibrium existing between p-dichlorobenzene sulfochloride and p-dichlorobenzenesulfonic acid in a mixture consisting of sulfuric acid and chlorosulfonic acid at 0° and 80°. The equilibrium constant was found to be 0.63 at 0° and 0.67 at 80°. The composition of the equilibrium mixture may be calculated with an accuracy of 1-2%. Attaining a state approaching that of equilibrium requires 20 or more hours at 0° but no more than 1 hour at 80°

These equilibrium constants indicate that the thermal effect of the conversion of the chloride into the sulfo acid is either zero or negligibly small.

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Received November 25, 1949.

THE REACTION OF ARYL SULFONAMIDES WITH AMINES

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The reactions of amides of the carboxylic acids with amines are well known; as a result of these reactions the amines that are constituents of the acid amide are replaced by the amines that are reagents in the reaction.

These reactions (aminolysis reactions) may be regarded as acylations of aromatic amines by acid amides.

An exchange reaction of this sort is effected very easily with urea, thiourea and their derivatives.

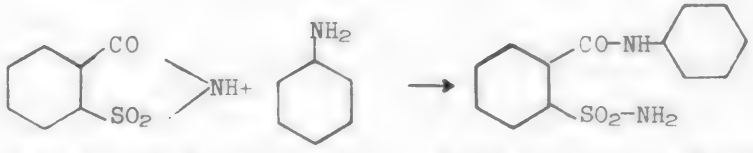
Braz, Livgunova, and Chemerisskaya [1] have worked out a similar method for producing sulfanilamide from aniline.

B.A.Porai-Koshits [2] made a detailed study of the reaction of phthalamic acids with aryl amides and demonstrated the reversibility of a reaction of this type in various instances.

The ease with which the reaction takes place in the phthalamic acids enabled Lesser [3] to secure p-nitroaniline by heating aniline to 120-130° with p-nitrophenylphthalamic acid.

The problem of the reaction of sulfonamides with amines is of considerable interest, inasmuch as the properties of the amide group in sulfonamides greatly resemble those of the amide group in carboxylic acids.

The aminolysis of mixed amides contaning a $-CO-NH-SO_2-$ group, however, is striking evidence of the high resistance of the $-HN-SO_2-$ amide bond to aminolysis. In all the numerous instances of the aminolysis of saccharin [4], for instance, we find the C—N bond ruptured while the N—S bond remains intact, as in:



There are no detailed investigations of the aminolysis of sulfonamides to be found in the literature. Most of the information on this problem is contained in the patent literature and refers to special cases, chiefly, heterocyclic derivatives and amides of sulfonic acids.

Bell [5] observed the splitting out of one aryl sulfonyl group, aryl sulfonyl piperidides being formed. Several other researchers have noted analogous tranformations [6].

In our endeavor to effect an exchange reaction between aryl sulfonamides and aromatic amines, we came up against the absence of any exchange reaction, to begin with, when sulfonamides are heated with free amines.

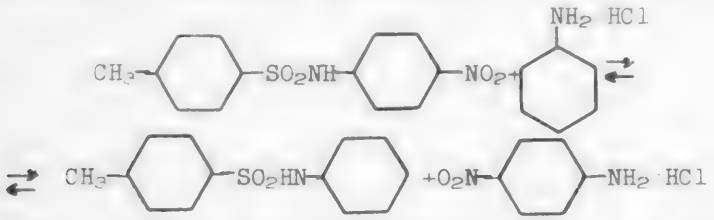
When p-toluenesulfo-p-nitroaniline was heated to temperatures ranging from 190-210° with aniline for 15 to 60 minutes for example, the reagents were recovered wholly unchanged. What is more, p-toluenesulfonamide does not

react with dimethyl-aniline at 190°, while sulfidine does not react with p--toluenesulfodiphenylamide at 200°.

In contrast thereto, we have found that the hydrochlorides of aryl amides react with sulfonamides and their N-substitution derivatives when heated for only a few minutes to a temperature above the hydrochloride s melting point.

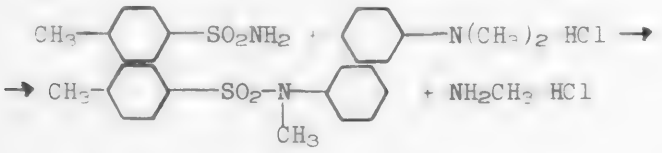
This highly interesting phenomenon which indicates that the presence of hydrogen chloride in the reaction mass is indispensable for the completion of the process, has also been observed by various authors in acylation with amides of carboxylic acids.

We have established that the exchange reaction between p-toluenesulfo-p--nitroaniline and aniline hydrochloride[1] is reversible:

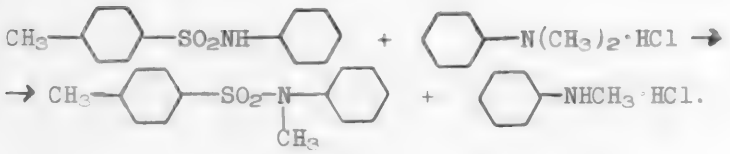


This reaction takes place whether both of the hydrogen atoms in the sulfonamide group are replaced (p-toluenesulfodiphenylamide with aniline hydrochloride) or one or both of the hydrogen atoms in the amine are replaced (p-toluenesulfonamide with dimethyl hydrochloride).

The reactions of the latter type



and



are of special interest, inasmuch as they are accompanied by side reactions in which triphenylmethane dyes are produced

We know [7] that the reaction of p-toluenesulfochloride with dimethylaniline yields crystal violet and di-(p-dimethylaminophenyl)-methane in addition to N-methylsulfanilamide. In view of the fact that the sulfonyl group $-SO_2-$ sometimes acts as an oxidant [8], it may be assumed (as has been done by S. I. Lurye and T. E. Rostkovskaya [9] for the reaction of sulfochlorides with dimethylaniline) that the CH_3^+ ion is oxidized, being converted into formaldehyde, condensation of the latter with dimethylaniline yielding triphenylmethane dyes.

Factors of phase equilibrium, wherever present, fundamentally affect the course of this reaction. When the reaction takes place in the liquid phase, we may observe the exit of the reaction products or of the reactants into the solid phase as a low-melting insoluble salt, or the exit of hydrogen chloride

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[1]) This reaction is accompanied by secondary oxidative-reducing processes in which nigrosinelike substances are formed (cf the experimental section).

into the gas phase whenever the salt is readily dissociated at the given temperature and pressure.

When N,N'-di-p-toluenesulfonylbenzidine is reacted with aniline hydrochloride, the resultant benzidine dihydrochloride (m.p. 385°) leaves the reaction zone as a solid, which shifts the equilibrium practically entirely to the right. On the other hand, when p-toluenesulfonanilide was heated to 320-340° with benzidine hydrochloride, neither di-p-toluenesulfonylbenzidine nor a monoacyl derivative was found among the products of the exchange reaction.

Moreover, the conversion of N-mono-p-toluenesulfonylbenzidine hydrochloride into di-p-toluenesulfonylbenzidine and benzidine hydrochloride by heating it above its melting point likewise proved to be irreversible.

The analogous behavior of the hydrochloride of the monosulfonyl derivative of benzidine when heated agrees with the difficulty of securing monosulfonyl derivatives of benzidine by reacting the latter with sulfochlorides. As Hopper and Alexander [10] have shown, a diacyl derivative is the principal reaction product even when a large excess of benzidine is present in the latter's reaction with benzene sulfochloride. We were unable to isolate a monoacyl derivative as a by-product of the synthesis of N,N'-di-p-toluenesulfonylbenzidine in pyridine.

Our results are listed in Table 1.

EXPERIMENTAL

1 Reaction of p-Toluenesulfo-p-nitroanilide With Aniline and Its Hydrochloride. 2.52 g of p-toluenesulfo-p-nitroanilide (synthesized in accordance with [11]), with a m.p. of 190°, and 2.96 g of freshly distilled anhydrous aniline were heated together to 180° for 25 minutes in a flask fitted with a reflux condenser. After the aniline had been driven off with steam, the residue was repeatedly extracted with hydrochloric acid. No p-nitroaniline was found in the extracts. The solid residue was dissolved in 10% NaOH; no p-toluenesulfonanilide was recovered from the resultant solution after it had been clarified with charcoal and acidulated with dilute hydrochloric acid. The original reagents were recovered in full.

Nordid heating 0.3 g of p-toluenesulfo-p-nitroanilide with 0.6 g of aniline to 195° for an hour result in the formation of the expected p-toluenesulfanilide.

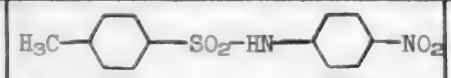
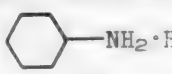
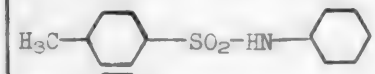
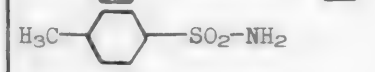
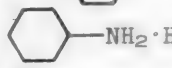
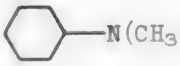
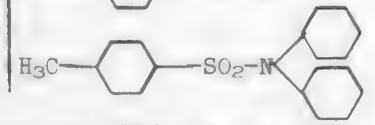
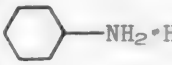
3.1 g of p-toluenesulfo-p-nitroanilide, 0.84 g of aniline, and 3.35 g of aniline hydrochloride were heated together to 200-220° for 20 minutes. The hydrochloric acid extracts were neutralized with soda, and the aniline was driven off with steam. The remaining solution was separated into two equal parts. One part was titrated with nitrite (after having been acidulated with concentrated hydrchloric acid) to determine the percentage of amines (the yield of p-nitroaniline was 0.2 g, or 13.6% of the theoretical, based on the anilide); the other part was chilled and a small amount of soda was added, yielding fine orange needles with a m.p. of 146° (after crystallization from alcohol); the mixed melting point with p-nitroaniline was 146°.

The solid residue left after the extraction with hydrochloric acid was washed with water and treated with 10% NaOH. The residue that was insoluble in the alkali was washed and dried and constituted a powder with a violet tinge, much of which dissolved in an aqueous solution of acetic acid and alcohol, turning the solution violet-red. The product was not investigated any further.

The alkaline extract (after decolorization with charcoal) was carefully acidulated with dilute hydrochloric acid. The initial fractions consisted of nothing but p- toluenesulfanilide (the m.p. of the product, as well as that of a fusion sample, was 102-103°); the yield was 0.6 g, hydrolytic cleavage by

TABLE 1

Reaction of Amides of Aromatic Sulfo Acids With Amides in the Presence of Hydrogen

Test No.	Reagents			Reaction conditions
	Original sulfonamide	Amine hydrochloride	Molar ratio of sulfonamide : amine	Temperature
1			1/3	197°
2			9/17	180–190
3			4/7	190–200
4			7/10	185–190
5			1/1.46	195

heating with 80% H_2SO_4 yielded aniline. The subsequent fractions were the unchanged p-toluenesulfo-p-nitroanilide.

The results of these tests are given in Tables 2 and 3.

TABLE 2

Effect of the Percentage of Aniline Hydrochloride Upon the Yield of p-Nitroaniline[1]

p-Toluenesulfo--p-nitroanilide, grams	Aniline, grams	Aniline hydrochloride, grams	Per cent yield of p-nitroaniline[2]
1.25	1.40	0.20	11.8
1.14	0.70	0.90	15.6
1.27	0.50	1.50	21.0
1.05	-	1.82	29.8

1) Temperature 200°, duration 15 minutes.

2) Based on the initial anilide.

2. Reaction of p-Toluenesulfonanilide With p-Nitroaniline and Its Hydrochloride.

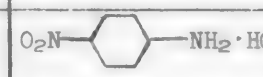
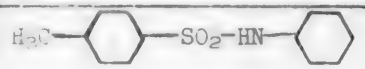
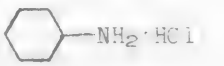
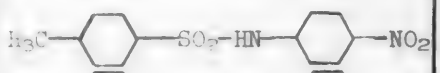
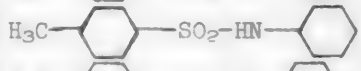
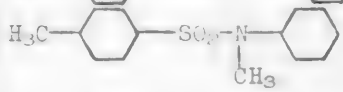
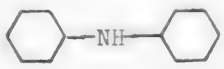
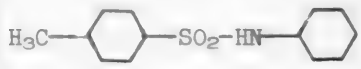
A finely pulverized mixture of 3.71 g of p-toluenesulfonanilide and 6.07 g of p-nitroaniline was heated for an hour to 205°. The reaction mass was extracted several times with 1:1 hydrochloric acid, and the extracts were neutralized with NaOH and distilled with steam, no aniline being found in the condensate. The residue was extracted with hydrochloric acid, but no p-toluenesulfo-p-nitroanilide was recovered, the p-toluenesulfonanilide (m.p. of the product 103° mixed m.p. 102°) being regenerated completely.

A current of anhydrous hydrogen chloride was passed through solution of 0.54 g of p-nitroaniline and 1 14 g of p-toluenesulfonanilide in 3 ml of ether until the solution was saturated. Then the ether was driven off, and the mixture was heated from 140 to 180° for 15 minutes, the temperature then being raised from 180 to 190° for another 15 minutes.

Processing of the reaction mass as specified above yielded 0.4 g of p--toluenesulfo-p-nitroanilide with a m.p. of 188° (54.5%, based on the reacted

TABLE 1 Continued

Chloride.

Time, Minutes	Reaction Products: Amine	Per cent yield[1]	Sulfonamide	Per cent yield of acylated product[1]
15		66.4[2]		60
15		-		54
15	(NH_4Cl)	-		50
15	(CH_3NH_2HCl)	-		17
20		-		37

[1] Yield in per cent of the theoretical, without allowing for regeneration of the original amide.

[2] Of the reacted sulfonamide.

TABLE 3

Effect of Temperature and Heating Time Upon the Product Yield in the Reaction of p-Toluenesulfo-p-nitroanilide With Aniline Hydrochloride

p-Toluene-sulfochloride, grams	Aniline hydro-chloride, grams	Temper-ature °	Heating time, minutes	Yield: p-Nitro-aniline[3]	P-Tolu-enesulfon-anilide[3]	Insoluble residue[4]	Re-generated p-toluene-sulfo-p-nitro-anilide[4]
1 166	1 03	190	6	15.2	15.0	0.9	82.0
1.6	1.42	190	15	23.8	17.6	2.0	70.0
1.17	1.04	190	30	20.5	20.0	2.6	67.5
0.98	0.87	197.5	15	27.0	24.0	8.0	60.2
2.0	1.78	205	15	20.2	16.5	40.5	35.6

[3] Per cent of the theoretical, based on the original anilide.

[4] Per cent of the initial anilide by weight.

p-toluenesulfonanilide). The mixed melting point was 168°., and 0.52 g of p-toluenesulfonanilide (m.p. 103°) was regenerated. The residue, insoluble in acids or alkalies, totaled 0.12 g.

3. Reaction of p-Toluenesulfonamide With Aniline Hydrochloride. A finely pulverized mixture of 0.28 g of p-toluenesulfonamide and 0.27 g of aniline hydrochloride was heated to 190-200° in a sealed tube for 15 minutes. The cooled mass was pulverized and then extracted with hot water. The aqueous extracts were faintly pink. When the combined aqueous extracts were chilled fine crystals with a m.p. of 124° settled out; the mixed melting point of the product and p-toluenesulfonamide was 136° after two recrystallizations from alcohol (decolorization with charcoal). The regenerated amide totaled 0.2 g.

The solid residue dissolved completely when gently heated in a 10% NaOH solution. Acidulating the solution with dilute hydrochloric acid after it had been processed with charcoal yielded 0.06 g of p-toluenesulfonanilide (50% of the theoretical, allowing for the regenerated amide). The m.p. was 102° after recrystallization from alcohol, the mixed melting point being 102°.

4. Reaction of p-Toluenesulfonamide With Dimethylaniline Hydrochloride. 1.2 g of p-toluenesulfonamide was added to 3 ml of freshly distilled anhydrous dimethylaniline,[1] saturated with anhydrous hydrogen chloride, and the mixture was heated to 185-190° in a sealed tube for 15 minutes. The contents of the tube were extracted with dilute hydrochloric acid. When soda was added to the yellow-green hydrochloric acid, it turned violet-blue. The blue residue was washed with water and heated with 30 ml of 10% NaOH over a water bath. A thin layer of a dark-blue oil settled to the bottom of the beaker, solidifying upon cooling. The foregoing change in color, which is characteristic of the dye crystal violet, justifies the assumption that in this experiment of ours crystal violet was produced, in additon to the "displacement" of the amine from the sulfonamide group.

The alkaline extract was cold filtered several times after a clear solution had been secured. Acidulating this solution threw down a precipitate that had a m.p. of 135-137° after crystallization from 80% alcohol (this being the m.p. of p-toluenesulfonamide) The yield of the pure product was 0.47 g.

The solidified dark-blue oil was recrystallized from a mixture of alcohol and acetic acid. This yielded 0.2 g of the colorless crystals of N-methyl-p--toluenesulfonanilide, with a m.p. of 94°. or 17% of the theoretical.

5. Reaction of p-Toluenesulfodiphenylamide With Aniline Hydrochloride. A pulverised mixture of 1.62 g of p-toluenesulfodiphenylamide [12] and 0.94 g of aniline hydrochloride was heated to 195° over an oil bath for 20 minutes. After the reaction mass had cooled, it was washed repeatedly with hot water, and then heated over a water bath with a 10% solution of sodium hydroxide. When the wash waters were chilled, a small quantity of diphenylamine settled out as colorless platelets with a m.p. of 54°.

When the alkaline extract was acidulated with hydrochloric acid and allowed to stand, colorless crystals settled out as needles with a m.p. of 102-104°: p-toluenesulfonanilide. The yield was 0.46 g, or 37% of the theoretical.

SUMMARY

Like the amides of carboxylic acids the amides of sulfo acids can be acylated by primary amines. The presence of hydrogen chloride as a salt of the amine introduced into the reaction is a prerequisite for acylation with amides of aromatic acids.

When amides of sulfo acids are acylated with tertiary amines one of the alkyl groups is split out.

[1]) The traces of aniline and monomethylaniline were eliminated from the dimethylaniline with phthalic anhydride.

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Received September 28, 1949

A MODIFIED SYNTHESIS OF 2-METHYL-4-AMINO-5-ETHOXYMETHYLPYRIMIDINE

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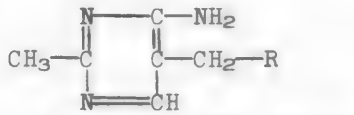
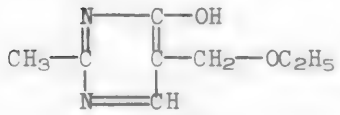
The principal intermediate product in the synthesis of aneurin is 5-R-methyl-4-amino-2-methylpyrimidine (I, where R = Cl, Br NH_2 HO or C_2H_5O). The substituted methyl group is usually obtained by converting 5-cyano- or 5-carbamido-methylpyrimidine into (I) after the ring had been closed [1,2]. This made the latter stages of the synthesis too long and expensive. Only few attempts have been made, however, to synthesize compounds of the (I) type directly Williams, for example, condensed the ethyl ester of 2-ethoxypropionic acid with ethyl formate securing the sodium salt of its 1-hydroxymethylene derivative (II), which could be converted, in turn, into a derivative of 4-hydroxypyrimidine (III) by treating it with acetamidine hydrochloride. The condensation of (II) with acetamidine produces an extremely small yield of the desired substance, however. The 4-hydroxyderivative of pyrimidine can be converted into the compound (I) (where R = C_2H_5O), required for the synthesis of vitamin B_1, in the next two stages.

Recently Chelintsev [3] succeeded in solving this problem. He produced 2-ethoxypropionitrile under extremely mild conditions. The acetate of the enol (V), secured from the derivative of (IV), reacted with two molecules of acetamidine to yield an amorphous product (apparently, 1-acetamidomethylene-2-ethoxypropionitrile), which was then regrouped into (I) by boiling it with alkali.

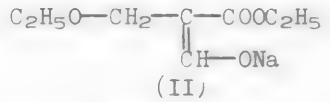


R = Cl, Br, NH_2, OC_2H_5

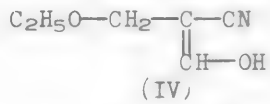
(I)



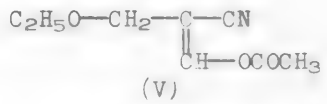
(III)



(II)

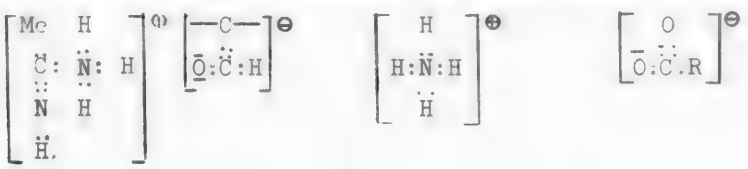


(IV)

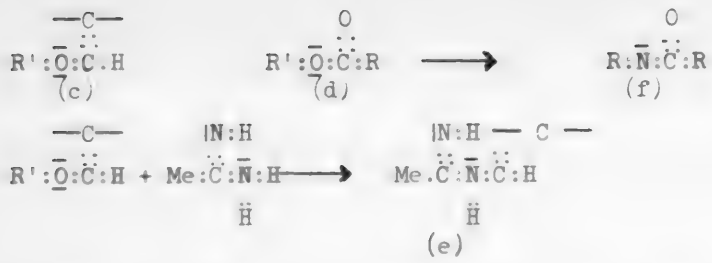


(V)

We attribute the low product yields secured in the Williams synthesis [5] to the fact that condensation is preceded by the formation of an acetamidine salt of sodium formylpropionate. This acetamidine salt—like the ammonium salts of organic acids—can be condensed only under extremely severe conditions. This assumption is supported by comparing the electronic configuration of the acetamide salt (III) with the configuration of an ammonium salt of an organic acid.



(a) (b)

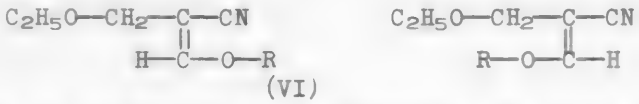


The esters of enols, on the other hand, cannot form salts with amines or amidines, but as they possess an electron structure that resembles that of acid esters, they can be readily converted into en-amines.

What is more, the esters and nitriles of alkoxy methylenemalonic acids are usually readily condensed with one molecule of acetamide in a single stage into the respective pyrimidines.

With these two facts in mind, we decided to employ Chelintsev's excellent method, using enolic ethers of formylethoxypropionitrile instead of the esters of the enols.

The sodium salt of (IB) was prepared by the Chelintsev method. It was identified by converting it into a p-nitrobenzoyl derivative. Only a single crystalline modification of this derivative was obtained, though cis and trans modifications are apt to result simultaneously from formylation, one of them being liquid in all probability. A very high yield of the methyl ester of the enol (V) was secured by reacting dimethyl sulfate with the condensation product of ethoxypropionitrile and ethyl formate, without isolating the sodium salt of (IV) in the pure state. The methylation product could be separated into fractions of different boiling points by fractional distillation. But each of these fractions exhibited nearly the same percentages of nitrogen and alkoxy groups, when recomputed in terms of a methoxymethylene derivative. Hence this broad boiling range was due to the presence of two geometrical isomers of the unsaturated compound (VI).



(VI)

Determination of the alkoxy groups indicated that only O-alkylation took place, no C-alkyl derivative being produced. Methylating the sodium derivative of acetoacetic ester under similar conditions yields only a C-methyl derivative. As we had assumed regarding the condensation of (IV) with acetamidine, it was only the high-boiling fraction that yielded the expected pyrimidine. The latter was isolated both as its well-known picrate and as the hitherto undescribed hydrochloride, m.p. 210°.

The ethyl ether of the enol (IV) was prepared by isolating the free hydroxymethylene derivative from its sodium salt, followed by processing it with ethyl orthoformate in the presence of benzenesulfonic acid. The resulting ethyl ether of the enol was then converted into pyrimidine (I) (R = ethoxyl).

We made several attempts to synthesize the intermediate product (VI), starting out with an inexpensive and readily available compound – glycerol. One approach involved the preparation of the diethyl acetal of 1-bromo-2-

ethoxypropionaldehyde (VII) from acrolein dibromide [7]. We tried to substitute the cyanogen group for the bromine in the acrolein to secure the diethyl acetal of (IV), but had no success, though we tested cyanides of various metals under all sorts of conditions. When we used aqueous-alcoholic solutions of sodium or potassium cyanide, the bromine was eliminated, true enough, but we did not manage to get the cyanogen group to enter.

On the other hand, we tried to prepare 1,3-diethoxy-2-hydroxy-2-cyanopropane (IX) from 1,3-dichlorohydrin, via 1,3-diethoxypropanol-2 [8] and 1,3-diethoxypropanone-2 (VII). (IX) could be converted into (VI), where R = C_2H_5, by splitting off one molecule of water. The tertiary hydroxyl group proved to be extraordinarily resistant to the action of various dehydrating agents. When we boiled it with acetic anhydride, we got a stable O-acetyl derivative, from which acetic acid could not be split off even by heating. The action of phosphorus pentoxide and phosphorus oxychloride in pyridine yielded only polymer products. Nor did oxalic acid prove suitable for this purpose.

Thus, despite the unsatisfactory results we secured when we started out with glycerol, the use of sodium formyl-2-ethoxypropionitrile enabled us to apply the Chelintsev synthesis to ethers of the enols, i.e., to 1-methoxy-methylene-2-ethoxypropionitrile. The latter can be converted in a single stage, by condensing it with one molecule of acetamidine into the respective pyrimidine derivative of (I), where R = C_2H_5O.

$C_2H_5O-CH_2-\underset{\underset{Br}{|}}{CH}-CH(OC_2H_5)_2$ (VII)

$C_2H_5O-CH_2-\underset{\underset{O}{\|}}{C}-CH_2-OC_2H_5$ (VIII)

$C_2H_5O-CH_2-\underset{\underset{CN}{\diagdown}}{\overset{\overset{HO}{\diagup}}{C}}-CH_2-OC_2H_5$ (IX)

EXPERIMENTAL

1-Methoxymethylene-2-ethoxypropionitrile (VI) (R = CH_3). A mixture of 83 g (0.84 mol) of ethoxypropionitrile and 90 g (1.216 mol) of ethyl formate was added a drop at a time, with agitiation and chilling with ice to 8-10°, to 23 g (1 gram atom) of sodium wire in 500 ml of benzene. The sodium dissolved in the course of 3 hours, the sodium salt of (IV) being formed. The mixture was allowed to stand for 3 days at 15°, after which 125 g (0.99 mol) of dimethyl sulfate was added drop by drop to the mixture, the temperature rising to 55°. Then the mixture was heated at 55° for 3 hours. After it had cooled, 125 g of sodium methyl sulfate was filtered out and washed with 150 ml of benzene. The filtrate was evaporated to dryness in vacuum, the residue being distilled at 5 mm. This yielded 3 fractions: 1) b.p. 70-96°, 36.5 g; 2) b.p. 96-112°, 48 g; and a residue of 12 g (a tar). Fractions 1 and 2 were combined and redistilled at 1 mm: 1) b.p. 64-71°, 30 g; 2) 71-92°, 17.6 g; and 3) b.p. 92-95°, 32.3 g.

Found %: Fraction 1 N 7.9; C_2H_5O 65.8; Fraction 2 N 8.6; C_2H_5O 59.3; Fraction 3 N 9.8, 9.6; C_2H_5O 59.2, 58.7. $C_7H_{11}O_2N$. Calculated %: N 9.95, alkoxy (to C_2H_5O), 63.8.

1-Ethoxymethylene-2-ethoxypropionitrile (VI) (R = C_2H_5). The sodium salt of formyl-2-ethoxypropionitrile was isolated by centrifuging and then processed with the calculated amount of sulfuric acid in absolute ether to secure the free hydroxymethylene derivative. 4.5 g of the latter was dissolved in 4.7 g of ethyl orthoformate, and the mixture was poured over 1.2 g of freshly dried

benzenesulfonic acid (at 140° and 5 mm). When the mixture was heated to 44°, a violent reaction set in. The mixture was allowed to stand overnight and then extracted with 15 ml of a 20% solution of potassium bicarbonate, the traces of excess ethyl orthoformate being eliminated in vacuum. The 5.33 g of residue was used in the ensuing ring-closure reaction without further purification.

Found %: C_2H_5O 59.3. $C_8H_{13}O_2N$. Calculated %: C_2H_5O 56.9.

1-(p-Nitrobenzoylhydroxymethylene)-2-ethoxypropionitrile (VI) R = p-$NO_2C_6H_4CO$). 11 g of the sodium salt of the hydroxymethlene compound, isolated by centrifuging (% Na found: 18.1; % Na calc. for $C_8H_8O_2NNa$. 15.3) was suspended in 100 ml of anhydrous benzene and 12.4 g of p-nitrobenzoyl chloride (1 mol per gram atom of sodium) was added to the ice-chilled suspension, so that the reaction was clearly exothermic. The mixture was agitated for 5 hours, 10 g of the salt being filtered out and extracted by agitating it with 100 ml of benzene for 5 hours. The filtrates were combined and evaporated to dryness, yielding 11.7 g of yellow crystals (60%, based on the nitrobenzoyl chloride). Recrystallization from 45 ml of benzene yielded 7 g (38%) of minute needles with a m.p. of 103-104°, the melting point rising to 109-110° after another recrystallization.

Found %: N 9.6. $C_{13}H_{12}O_5N$. Calculated %: N 10.1.

2-Methyl-4-amino-5-ethoxymethylpyrimidine (I) (R = C_2H_5O). 1) A mixture of 2.82 g (0.02 mol) of the methyl ether of the enol (VI) (Fraction 3) and 1.16 g (0.02 mol) of acetamidine was allowed to stand in 20 ml of absolute alcohol for 24 hours. Then the yellowish reaction mixture was evaporated in vacuum and processed with a solution of 4.6 g (0.02 mol) of picric acid in 80 ml of hot water. This yielded 5.3 g of the picrate (66%), m.p. 165-175°. Recrystallization from 120 ml of water plus 40 ml of alcohol yielded 3.25 g of the analytically pure substance with a m.p. of 181-183° (the literature gives the m.p. as 181°). Alkaline decomposition, followed by extraction with chloroform, yielded the free base, with a m.p. of 90°.

2) 30 ml of a sodium ethylate solution, prepared from 0.92 g (0.04 gram atom) of sodium, was added at room temperature to a solution of 3.8 g (0.04 mol) of acetamidine hydrochloride and 5.64 g (0.04 mol) of the methyl ether of (VI) (Fraction 3) in 40 ml of absolute alcohol. After the mixture had stood overnight at 20°, the sodium chloride was filtered out and the filtrate was evaporated in vacuum at 40°. The 7.9 g of residue left after the solvent had been evaporated was dissolved in 50 ml of anhydrous chloroform; the solution was filtered, evaporated to dryness, redissolved in 60 ml of anhydrous ether and refiltered, an excess of hydrogen chloride in absolute ether finally being added to precipitate the hydrochloride of (I). The yield was 4.9 g (61%), with a m.p. of 196-197°, which was raised to 209° after recrystallization from butanol.

Found %: N 20.5; Cl 18.1. $C_{18}H_{14}ON_3Cl$. Calculated %: N 20.6; Cl 17.5.

3) The condensation was performed by the method described above, with benzene replacing the chloroform and anhydrous hydrogen chloride being passed through the ice-chilled benzene solution. The 14.1 g of the methoxymethylene derivative yielded 11.9 g of the crude hydrochloride of (I), which was recrystallized from 80 ml of n-butanol. The yield was 8.8 g, with a m.p. of 202-204°.

4) 1.624 g (0.0105 mol) of the ethoxymethylene derivative was processed for 24 hours with 0.64 g of acetamidine (0.011 mol) in 11 ml of absolute alcohol. The 1.64 g of oil left after vacuum distillation was poured into 60 ml of a

boiling aqueous solution of 3.5 g of picric acid. This yielded 2.83 g of the picrate, with a m.p. of 182°, the mixed melting point with the picrate prepared by Chelintsev's method exhibiting no depression.

Condensation of 1-acetoxymethylene-2-ethoxypropionitrile with acetamide. 8.45 g of acetoxymethylene-2-ethoxypropionitrile dissolved in 150 ml of benzene was added to a chilled acetamide solution, prepared with 9.5 g of acetamide hydrochloride, and 2.3 g of sodium in 40 ml of absolute alcohol, and the mixture was allowed to stand for 2 days at room temperature. Then the solvent was evaporated in vacuum, and 15 ml of acetone was added to the residue, which was then brought to a boil. This yielded 3.3 g of a crystalline precipitate with a m.p. of 162-165°. Its analysis yielded figures resembling those calculated for acetamidine acetate.

Found %: N 22.9. $C_4H_{10}O_2N_2$. Calculated %: N 23.7.

The residue of the acetone mother liquor was a light hyaline material (10.2 g), which produced a high yield of 2-methyl-4-amino-5-ethoxymethylene-pyrimidine under the conditions described by Chelintsev [3] or by simple sublimation at 0.04 mm.

Reaction of 1,1,3-triethoxy-2-bromopropane with cyanides. 1) 21 g of the bromoacetal and 4.1 g of sodium cyanide were dissolved in a mixture of 20 ml of alcohol and 5 ml of water, 1.8 g of sodium iodide was added, and the mixture was stirred for 12 hours at room temperature. The solvent was driven off in vacuum, the residue was diluted with ether, the ether was driven off, and the residue was distilled in vacuum. The only product recovered was the unchanged bromoacetal. 2) 41 g (0.16 mol) of the bromoacetal was heated by the Uhle method [10] to 75° for 2.5 hours with 10.5 g of potassium cyanide and 3.5 g of sodium iodide in a mixture of 40 ml of alcohol and 9 ml of water. The subsequent treatment was the same as in Test 1. Distillation yielded the following: Fraction 1: 6.4 g, b.p. 110-125° (24 mm) (% N: 0.3, % Br: 9.95 found : %N: 7.0, % Br:0 calculated for the acetal cyanide; % Br calculated from the initial bromine derivative:31.3); Fraction 2: 15.2 g, b.p. 125-127° (24 mm) (%N:0.2, %Br:11.3 found); Fraction 3; 2.2 g, b.p. 132-135° (24 mm) (%N:0.3, %Br:30.8 found). Fractions 1 and 2 were a mixture of the bromoacetyl and a hydroxyacetal, while Fraction 3 was the unchanged bromoacetal. 3) 18 g of the bromoacetal was boiled for 10 hours with 6.3 g of cuprous cyanide. The unchanged bromoacetal, plus a tarry residue was recovered.

1,3-Diethyoxypropanone-2 (VIII). A mixture of 450 g of concentrated sulfuric acid and 115 ml of water was added a drop at a time during the course of 8 hours to a solution of 340 g of diethylyne (1,3-diethoxypropanol-2) and 375 g of sodium bichromate in 225 ml of water. The same treatment as that described for dichloropropanone yielded 200 g of 1,3-diethyoxypropanone-2, with a b.p. of 95-100° (20 mm) [11].

1,3-Diethoxy-2-hydroxy-2-cyanopropanone (IX). 14 g of the ketone was agitated for half an hour with a freshly prepared bisulfite solution, made with 6.4 g of sulfur dioxide and 4 g of caustic soda in 40 ml of water. The resultant oil was extracted with 50 ml of ether and the ether extract desiccated with calcium chloride. 2 ml of the 57 ml of the bulk ether solution was analyzed, finding 0.035 g N. The quantitative conversion of the ketone should have yielded 0.048 g N. Hence the yield of the cyanohydrin from the ketone totaled 73%. The pure cyanohydrin was not isolated to avoid its decomposition.

1,3-Diethoxy-2-acetoxy-2-cyanopropane was prepared from the above-mentioned ether solution by adding 20 ml of acetic anhydride, evaporating the ether,

and boiling the reaction mixture for an hour. Distillation yielded 4.9 g of an oil, b.p. 104-106° (5 mm) that contained no active hydrogen and gave no precise analytical figures for an acetyl derivative. All endeavors to split off acetic acid met with failure.

Found %: N 6.6. $C_{10}H_{17}O_4N$. Calculated %: N 6.5.

The authors wish to express their gratitude to O. Fuchs for his assistance and to the analytical laboratory of the 'Quinoin' factory for having made the analyses.

SUMMARY

The synthesis of pyrinimide by the Chelintsev method from esters of enols has been applied to enolic ethers the pyridine ring closure taking place in a single stage, using 1 mol of acetamidine.

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Received February 1, 1950.

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DI- AND TRIPYRIDYLMETHANE DYES

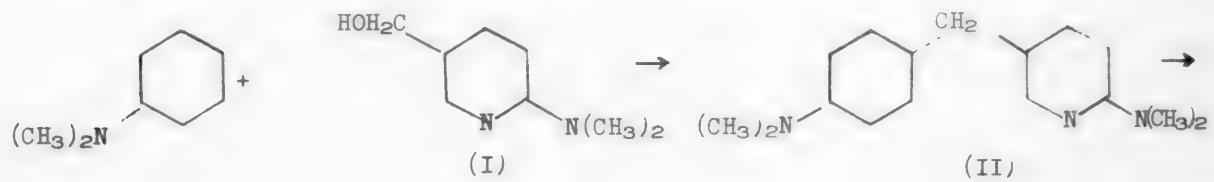
IV. MONOPYRIDINE ANALOGS OF DIPHENYLMETHANE DERIVATIVES

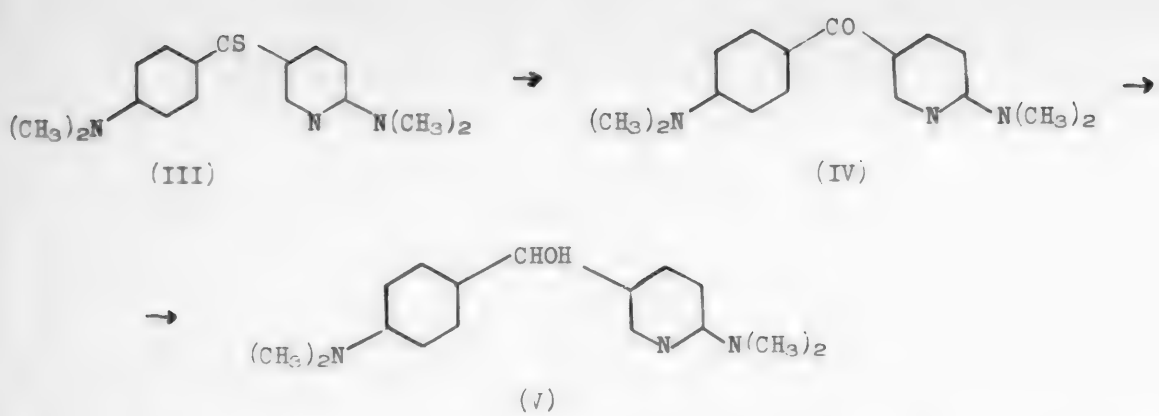
V. M. Berezovsky

Of the pyridine analogs of the triphenylmethane dyes, the only true dyes are those possessing three auxochromic groups at the para position [1]. Analogs that possess two auxochromic groups in the Pyridine ring, such as the analogs of Michler's hydrol and of the carbinol base of malachite green, do not yield dyes when they form salts [2,3]. The present research had as its objective the synthesis of mixed pyridylphenylmethane compounds especially a monopyridine analog of Michler's hydrol (V), and a study of its color. We proposed to [illegible] this compound by condensing an alkyl aminopyridylcarbinol with an aromatic amine and then oxidizing the condensation product.

In a previous report [4] we have shown that the α-pyridine tertiary amines condense with formaldehyde at the β' position, yielding dipyridylmethane derivatives. This reaction may be thought of as occurring in two phases: at first one molecule of the amine combines with one molecule of formaldehyde to form a dialkyl aminopyridylcarbinol, which then reacts with a second molecule of the amine to form a dipyridylmethane derivative.

This concept of the reaction mechanism makes it possible for di-(2-dimethylamino-5-pyridyl)-methane [2], the principal product of the peculiar reaction between α-aminopyridine and formaldehyde in the presence of formic acid, to be formed via 2-dimethyl-aminopyridine. If this is so, then the reaction products should include 2-dimethyl-amino-5-pyridylcarbinol (I), one of the components we require for synthesizing the monopyridine analog of Michler's hydrol. As a matter of fact, we recovered a small quantity of this tertiary aminopyridylcarbinol by refractionating the first runnings of the major fraction of di-(2-dimethylamino-5-pyridyl)-methane (VIII). At 154-157° (5 mm) we secured an oil, from which leaflets with a m.p. of 45.5° were obtained. The presence of a hydroxyl group in this substance was demonstrated by its reaction with metallic sodium; its analysis indicated that it was 2-dimethylamino-5-pyridylcarbinol (I), which proves conclusively that the well-known di-(2-dimethylamino-5-pyridyl)-methane is synthesized by condensing it with 2-di-methylaminopyridine. We condensed 2-dimethylamino-5-pyridylcarbinol with dimethylaniline in formic acid and secured a high yield of 2-dimethylamino-5-pyridyl-(p-dimethylaminophenyl)-methane (II). When the latter compound was oxidized with a dilute acid solution of lead dioxide, the intense green color of a salt of the monopyridine analog of Michler's hydrol appeared, but we did not have enough of the material to isolate it in the pure state. We therefore synthesized the monopyridine analogs of Michler's hydrol and ketone by the usual method [2], as follows:





(III) (IV) (V)

The thione (III) was prepared by fusing the compound (II) with sulfur in vacuo at 175°, the yield being 41%. Hydrolyzing the thione with dilute hydrochloric acid yielded the ketone (IV) almost quantitatively. Reducing the ketone with sodium amalgam in alcoholic solution gave us a high yield of the carbinol (V) The structure of the carbinol is unmistakable from the method used in its synthesis; it was established by analysis. The carbinol turns glacial acetic acid an intense blue-green and colors dilute hydrochloric acid a violet-blue.

TABLE

Properties of the Pyridine Analogs of Tetramethyldiaminodiphenylmethane and Its Derivatives

Tetramethyldiamino derivatives	Melting point	Color in solution			Picrate melting point.
		Concentrated sulfuric acid	Dilute sulfuric acid	Glacial acetic acid	
Diphenylmethane.....	91°	colorless	colorless	colorless	178°
Pyridylphenylmethane.....	82	colorless	colorless	colorless	199 [1]
Dipyridylmethane.....	85	colorless	colorless	colorless	227 [1]
Diphenylthione.....	202-204	—	—	Green	—
Pyridylphenylthione.....	187-189	Intense orange	Brown-orange	Orange	—
Dipyridylthione.....	167.5	Intense red-orange	Violet	Lemon-yellow	—
Diphenyl ketone.....	173	colorless	colorless	Lemon-yellow	156-157
Pyridyl phenyl ketone....	164-165	Yellow	Yellow	Yellow	180-182
Dipyridyl ketone.....	169-170	Yellow	Light-yellow	Yellow	184-185
Diphenylcarbinol.....	96 or 103	Yellow	Sky-blue	Very intense violet blue	—
Pyridylphenylcarbinol....	124	Intense orange	Violet-blue	Intense blue-green	147 [1]
Dipyridylcarbinol.....	154	Intense purple	colorless	colorless	176 [1]

[1]) With decomposition.

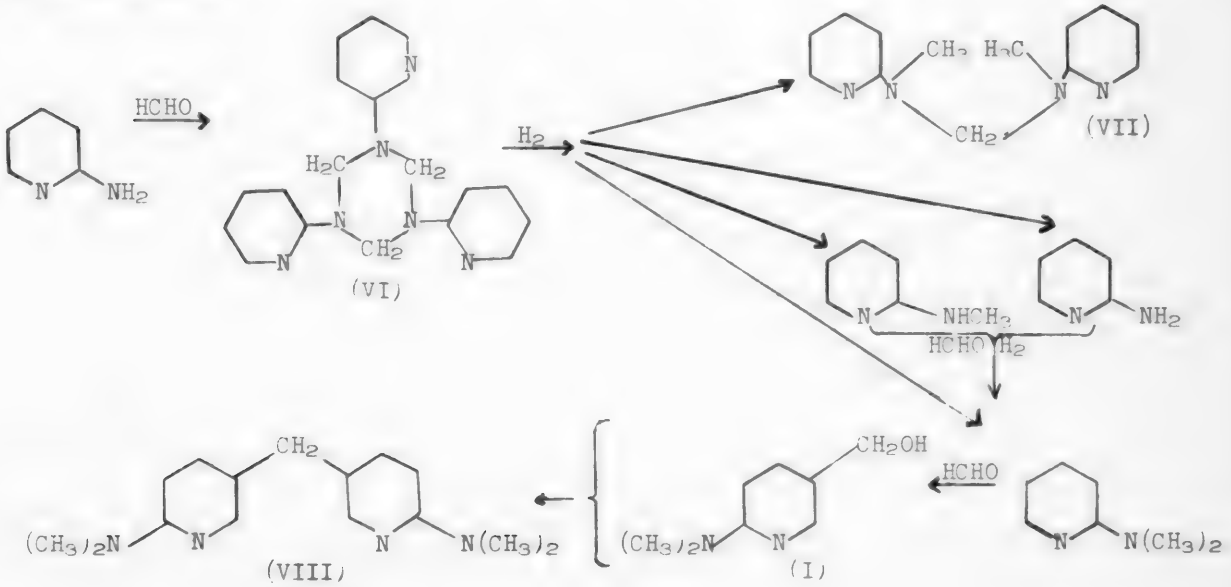
Thus the well-known absence of color in dipyridylmethane and dipyridylphenylmethane derivatives possessing two auxochromic groups at the para position of the pyridine rings is complemented by the presence of color in pyridylphenylmethane dyes that have two auxochromic groups at the para position in the pyridine and benzene rings.

The properties of dipyridylmethane derivatives and of the new derivatives of pyridylphenylmethane are listed in the table.

In our analysis of the first runnings of the di- -dimethylamino-5-pyridyl)-methane fraction, we secured a substance with the formula $C_{13}H_{16}N_4$ as needles with a m.p of 139-140° (after several recrystallizations from alcohol and gasoline). Since this substance does not react with p-nitrobenzoyl chloride and, hence is not dimethyldiaminodipyridylmethane, we assigned it the other possible structure, namely, di-(2-pyridylmethylamino)-methylene (VII). A substance with the same formula, $C_{13}H_{16}N_4$, in the form of needles with a m.p of 132-133° (after crystallization from ligroin), identified as di-(2-pyridylmethyl-amino)-methylene, was secured together with 2-aminopyridine and 2-methylaminopyridine, when 1,3,5-tri-(2'-pyridyl)-trimethylenetriamine was boiled with formic acid [5]

When we reacted 2-aminopyridine with formaldehyde in formic acid, we also secured a small amount of an amine that distilled with steam, which was identified as 2-di-methylaminopyridine from its boiling point, the absence of any reaction with acetic anhydride, its analysis, and its specific odor.

Our findings indicate that the reaction of 2-aminopyridine with formaldehyde in reducing agents proceeds as follows. At the beginning, the action of formaldehyde upon 2-aminopyridine produces a trimer of the hypothetical Schiff base $NC_5-H_4N=CH_2$ as 1,3,5-tri-(2'-pyridyl)-trimethylenetriamine (VI), which is broken down into 2-dimethylaminopyridine, 2-aminopyridine, 2-methylaminopyridine, di-(2-pyridyl-methylamino)-methylene (VII), and other compounds when reduced by formic acid or active hydrogen. All these products likewise end up as 2-dimethylaminopyridine as the result of methylation and reduction. This principal product of the first phase of the reaction



condenses with a molecule of formaldehyde to yield 2-dimethylamino-5-pyridylcarbinol (I), and it is the combination of the latter with another molecule of 2-dimethylamino-pyridine that yields di-(2-dimethylamino-5-pyridyl)-methane (VIII).

Thus the aminopyridine is first methylated, and only thereafter is it condensed with the aldehyde at the para position to the amino group to form a dipyridylmethane derivative. This course of the reaction may be due to the low activity of the hydrogen atom attached to the carbon atom in the para position to the alpha amino group of the pyridine ring, as compared to its aromatic analog. We have witnessed a similar low activity of the hydrogen atom in this position in the condensation of 2-dimethylamino-pyridine with benzaldehyde and other compounds [3].

EXPERIMENTAL

Action of formaldehyde upon 2-aminopyridine in formic acid. A mixture consisting of 1000 g of formic acid (sp. gr. 1.2), 470 g of 2-aminopyridine, and 2400 ml of formalin was refluxed to a gentle boil for 16 hours. Then the excess formalin was driven off with steam. The remaining solution was neutralized with a 40% sodium hydroxide solution until its reaction was alkaline, an oily layer separating out. The mixture was then distilled with steam, the aqueous distillate being extracted with benzene. The solvent was driven off, and the extract residue was boiled for an hour with 5 g of acetic anhydride, after which the mixture was fractionated in vacuo. Up to 100° (14 mm) a mixture of 2-dimethylaminopyridine and acetic anhydride was distilled, it being processed with a sodium hydroxide solution and then extracted with benzene. The solvent was driven off, and the 2-dimethylaminopyridine was distilled in vacuo. All of it distilled at 88° (15 mm) 2 8 g yield.

2.920 mg substance: 0.600 ml N_2 (22°, 745 mm). Found %: N 23.30. $C_7H_{10}N_2$. Calculated %: N 22.94.

The oily layer of the base left after the steam distillation was dissolved in 400 ml of benzene and separated from the aqueous layer. The solvent was driven off, and the base was distilled in vacuo.

First runnings, b.p. up to 206° (2 mm), 85 g; the major fraction, b.p. 206-208° (2 mm), 320 g, was di-(2-dimethylamino-5-pyridyl)-methane (VIII); the m.p. of the crude product was 72-77°. Recrystallization from alcohol yielded colorless leaflets, m.p. 84-85°.

After the first runnings had been allowed to stand for a long time, 10 g of crystalline di-(2-dimethylamino-5-pyridyl)-methane was recovered, and the liquid portion of the first runnings was fractionated in vacuo. Six fractions were collected: Fraction 1 – b.p. 92-94° (15 mm), 4 g; Fraction 2 – b.p. 104-120° (20 mm), 16 g, an oil that crystallized upon standing, yielding 3.9 g of 2-aminopyridine with a m.p. of 57-58°; Fraction 3 – b.p. 120-168° (20 mm), 2 g (intermediate); Fraction 4 – b.p. 154-157° (5 mm), 16 g, a thick oil that solidified when strongly chilled. The crystals were filtered out and washed thoroughly with benzene (130°) – yield 7 g. Recrystallization from an ether – petroleum ether (35-50°) mixture yielded colorless leaflets with a m.p. of 45.5°. This substance is highly hygroscopic and freely soluble in methanol, ethyl alcohol, butyl alcohol, chloroform, ether, and benzene. Reacting a benzene solution of the substance with metallic sodium liberated hydrogen. The substance is 2-dimethylamino-5-pyridylcarbinol (I).

3.481 mg substance: 8.092 mg CO_2; 2.520 mg H_2O; 3.242 mg substance: 7.532 mg CO_2; 2.345 mg H_2O; 3.470 mg substance: 0.589 ml N_2 (17°, 739 mm); 0.0058 g substance; 0.1107 g camphor: Δt 18.1°. Found %: C 63.44, 63.40; H 8.10, 8.09; N 18.99; M 159 (by Rast-Duran) $C_8H_{12}ON_2$. Calculated %: C 63.13; H 7.95; N 18.41; M 152.

The picrate of 2-dimethylamino-5-pyridylcarbinol was synthesized and recrystallized from alcohol – yellow prisms, m.p. 165° (with decomposition).

Fraction 5 – b.p. 157-205° (5 mm), 13 g (the bulk of the fraction distilling below 160°), a thick oil consisting chiefly of 2-dimethylamino-5-pyridylcarbinol, which crystallized in part upon standing. Fraction 6 – b.p. 205-233° (5 mm), 2.7 g, a thick oil nearly all of which crystallized. The crystals were filtered out and thoroughly squeezed out; repeated recrystallization from alcohol and then from gasoline yielded stubby needles, m.p. 139-140°. The substance was not benzoylated by p-nitrobenzoyl chloride. This substance was identified as di-(2-pyridylmethylamino)-methylene (VII).

3.270 mg substance: 8.227 mg CO_2; 2.100 mg H_2O; 3.950 mg substance: 0.860 ml N_2 (20°, 751 mm); 0.0037 g substance: 0.1004 g camphor: Δt 7.7°. Found %: C 68.66; H 7.18; N 24.52; M 238. $C_{13}H_{16}N_4$. Calculated %: C 68.38; H 7.07; N 24.55; M 228.

Condensation of 2-dimethylamino-5-pyridylcarbinol with 2-dimethylaminopyridine. A mixture consisting of 1 g 2-dimethylamino-5-pyridylcarbinol, 1.7 g of 2-dimethylaminopyridine, and 4 g of formic acid (sp. gr. 1.2) was refluxed for 7 hours. Then the mixture was diluted with water and neutralized with a sodium hydroxide solution, the excess dimethylaminopyridine being driven off with steam. When it cooled, the oily residue crystallized; it was separated from the aqueous solution and dried. This yielded 1.3 g (77% of the theoretical) of di-(2-dimethylamino-5-pyridyl)-methane (VIII), m.p. 72-78°. The substance had a m.p. of 84-85° after recrystallization from ligroin; the mixed melting point with known di-(2-dimethylamino-5-pyridyl)-methane exhibited no depression.

12.07 mg substance: 2.264 ml N_2 (21°, 753 mm): Found %: N 21.63. $C_{15}H_{20}N_4$. Calculated: % N 21.86.

2-Dimethylamino-5-pyridyl-(p-dimethylaminophenyl)-methane (II). 9 g of 2-dimethylamino-5-pyridylcarbinol, 15.3 g of dimethylaniline, and 36 g of formic acid (sp. gr. 1.2) were refluxed together for 7 hours. Then the mixture was neutralized with sodium hydroxide, the excess dimethylaniline being driven off with steam. The oily residue crystallized upon cooling; this yielded 13.6 g (94% of the theoretical) of a granulated precipitate, which was recrystallized from petroleum ether. The 2-dimethyl-amino-5-pyridyl-(p-dimethylaminophenyl)-methane was isolated as colorless leaflets, m.p. 82°. The substance is soluble in alcohol, though practically insoluble in water; it yields a colorless solution in concentrated sulfuric acid, the solution turning violet-blue when a crystal of potassium bichromate is added.

14.08 mg substance: 2.03 ml N_2 (20°, 756 mm). Found %: N 16.71. $C_{16}H_{21}N_3$. Calculated %: N 16.46.

The picrate of 2-dimethylamino-5-pyridyl-(p-dimethylaminophenyl)-methane was prepared from alcohol as yellow leaflets, m.p. 199° (with decomposition).

2-Dimethylamino-5-pyridyl-(p-dimethylaminophenyl)-thione (III). 2.5 g of the methane derivative (II) and 0.7 g of sulfur were heated to 170-175° in a 5-10 mm vacuum for 6 hours on an oil bath. Hydrogen sulfide was evolved during the reaction, its evolution ceasing almost entirely toward the end of heating. Then 5 ml of ethyl acetate was added to the raspberry-red solution, the thione soon beginning to crystallize. The next day the Bordeaux red prisms, with a dark-violet metallic tinge, were filtered out and washed with methanol. This yielded 1.16 g of the thione (41% of the theoretical), which was pure enough to be used in the following reaction. Several recrystallizations from absolute alcohol yielded 2-dimethylamino-5-pyridyl-(p-dimethylamino-phenyl)-thione, m.p. 187-189°. The substance dissolved in

concentrated sulfuric acid, turning it a bright yellow, which turned into a dull brownish orange when it was highly diluted; it dissolved in strong hydrochloric acid, coloring the solution brown-red.

3 921 mg substance: 0 509 ml N_2 (22°, 754 mm) Found %: N 14 90. $C_{16}H_{19}N_3$. Calculated %: N 14.72.

2-Dimethylamino 5-pyridyl-(p-dimethylaminophenyl) ketone (IV). 1.16 g of the crude thione (III) was dissolved in 10 ml of 10% hydrochloric acid and refluxed for 45 minutes, hydrogen chloride being evolved during the reaction. The brown-yellow solution was filtered, and a 20% solution of sodium hydroxide was added, precipitating the ketone, which was filtered out, washed with water, and dried. This yielded 1 09 g of the ketone (a nearly quantitative yield) Recrystallization from 1:7 alcohol yielded 0.87 g of the 2-dimethylamino-5-pyridyl-(p-dimethyl-aminophenyl) ketone as lustrous brownish-yellow leaflets, m.p 164-165°. The yield of the ketone (IV) from the methane derivative (II) was 33% of the theoretical.

10 87 mg substance: 1 51 ml N_2 (22°, 758 mm) Found %: N 16.03 $C_{16}H_{19}ON_3$. Calculated %: N 15.60.

The picrate of 2-dimethylamino-5-pyridyl-(p-dimethylaminophenyl) ketone was prepared from alcohol and recrystallized from an acetone-alcohol mixture as dark-yellow prisms, m.p. 180-182°

2-Dimethylamino-5-pyridyl-(p-dimethylaminophenyl)-carbinol (V). 0.5 g of the ketone (IV) was dissolved in 35 ml of 96% alcohol, and 7 g of 3% sodium amalgam was gradually added to the boiling solution After the solution had been refluxed for 3 hours and had become nearly totally colorless, it was filtered and reduced to 4 ml, and 12 ml of water was added, 0 48 g of a flocculent precipitate was thrown down, filtered out, and dried Recrystallization (dissolution in 1 ml of alcohol and adding 4 ml of ether) yielded the 2-dimethylamino-5-pyridyl-(p-dimethylaminophenyl)-carbinol as nearly colorless elongated prisms, m.p 124°. The carbinol colored concentrated sulfuric acid orange; a highly dilute solution of hydrochloric acid turning violet-blue The carbinol colored glacial acetic acid a bright blue-green.

11 05 mg substance: 1 49 ml N_2 (20°, 756 mm); 13.27 mg substance: 1.79 ml N_2 (24°, 755 mm) Found %: N 15.63, 15 43 $C_{16}H_{21}ON_3$. Calculated %: N 15.49.

The picrate of 2-dimethylamino-5-pyridyl-(p-dimethylaminophenyl)-carbinol was prepared from alcohol and recrystallized from an acetone-alcohol mixture as greenish-yellow prisms, m.p. 147° (with decomposition).

SUMMARY

1. Several pyridylphenylmethane derivatives have been synthesized and their structure established.

2 It has been found that the monopyridine analogs of diphenylmethane dyes that have two auxochromic groups at the para position are colored.

3. The mechanism involved in the formation of di-(2-dimethylamino-5-pyridyl)-methane from 2-aminopyridine and formaldehyde in the presence of reducing agents has been established: the first reaction is a condensation to a trimethylenetriamine derivative, which is reduced to dimethylaminopyridine, it being only the latter that condenses with formaldehyde via a pyridylcarbinol into a dipyridylmethane derivative.

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Received December 25, 1949.

CHEMICAL STRUCTURE AND PARASITICIDAL ACTIVITY

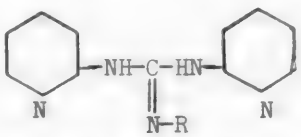
XI. DERIVATIVES OF DIPYRIDYLGUANIDINE

M. B. Braude and K. S. Topchiev

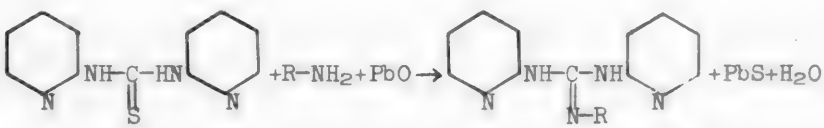
Various guanidine derivatives have been studied by several authors, who have commented on the significance of these compounds for some problems of biology and medicine.

Galegine [1] and streptomycin [2], are interesting examples of complex natural biologically active products whose molecules contain guanidine groups. Bischoff [3] and Bischoff and his co-workers [4] studied synthetic derivatives of guanidine that contained heterocyclic components (diguanylpiperazine and diguanylpiperidine). Paludrine is an example of the high antimalarial effectiveness of biguanidine derivatives [5].

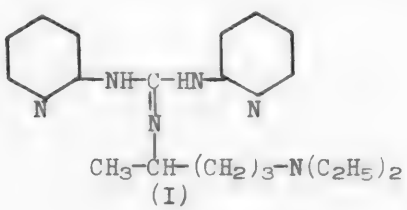
More than fifteen years ago we made a study of new guanidine derivatives [6]. We found that some of the derivatives of dipyridylguanidine we had synthesized, which were previously unknown, were powerful local anesthetics. That paper of ours made it possible to synthesize alkyl and aryl substitution derivatives of symmetrical dipyridylguanidine, their general formula being:



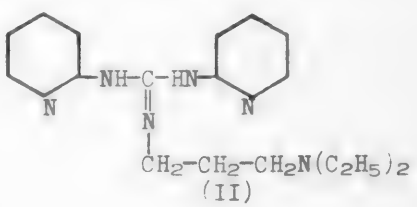
prepared by reacting the respective dipyridylthiourea with an amine in the presence of a desulfurizing agent:



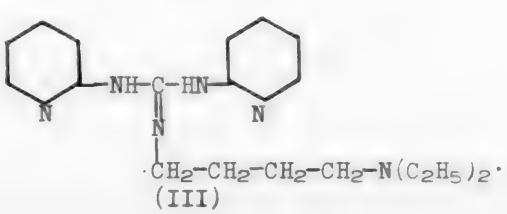
These earlier researches of ours have made it possible to synthesize the substances (I), (II), and (III) in the present research to test their antimalarial activity:



(I)

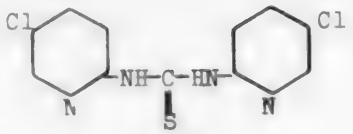


(II)



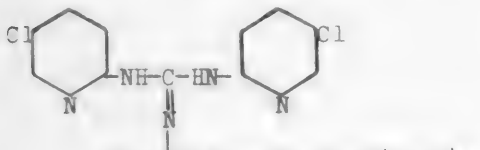
(III)

We continued along these lines, synthesizing the hitherto unknown sym-di-(5-chloropyridyl)-thiourea (IV):

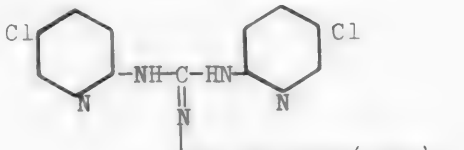


(IV)

which was then converted into the corresponding dialkyl-aminoalkyl substitution derivatives of guanidine (V) and (VI):



(V)



(VI)

When we synthesized the substitution derivatives (I), (II), and (III) of dipyridylguanidine from the respective dipyridylthiourea, the latter had a m.p. of 147°, and its other properties agreed with those described in the literature [7,8]. The dipyridylthiourea reactions described above yielded, in addition to the substitution derivatives (I) and (III) of guanidine, a crystalline substance with a m.p. of 227°, whose percentages of carbon, hydrogen, nitrogen, and sulfur were those of dipyridylthiourea, with a m.p. of 147°, although its properties were entirely different. The structure of this substance has not been investigated as yet.

The substitution derivatives (I), (II), and (V) of dipyridylguanidine described herein proved to be inactive when tested with bird malaria.

EXPERIMENTAL

Sym-di-2-pyridyl-(4'-diethylamino1-1'-methylbutyl)-guanidine (I). The initial dipyridylguanidine was prepared in accordance with the procedure described in a paper by one of the present authors [6], the yield being 74.6% of the theoretical, based on α-aminopyridine. The synthesizied thiourea corresponded to the form described, with a m.p. of 147-148° [8]. The reaction of dipyridylthiourea with 1-diethylamino-4-aminopentane and the desulfurizer PbO was carried out in a flask fitted with a reflux condenser and a stirrer equipped with a hermetic seal. 4.6 g of dipyridyl-thiourea was heated and stirred in 50 ml of absolute alcohol until it dissolved, and then 4.6 g of 1-diethylamino-4-aminopentane (50% excess over the theoretical) and 40 g of pulverized basic lead carbonate were added. The white suspension turned black within 20-30 minutes; after 8 hours of heating to 70° the filtrate did not change the white color of a fresh batch of basic lead carbonate. Then the alcohol was driven out of the alcoholic filtrate, the cooled residue being an oil containing a minute quantity of shining white crystals. The crystals were separated from the oil by adding ether, filtered out, and washed with ether. This yielded 0.5 g of a crystalline substance, m.p. 220-225°. This crystalline substance contained sulfur and was freely soluble in alcohol and hot water, slightly soluble in cold water, and ether. After recrystallization from water the substance had a m.p. of 226-227°, its analysis being as follows:

3.109 mg substance: 6.587 mg CO_2; 1.026 mg H_2O. 3.081 mg substance: 6.525 mg CO_2; 1.008 mg H_2O. 2.193 mg substance: 0.474 ml N_2 (18.5°, 733 mm). Found %: C 57.82,

57.80; H 3.69, 3.66; N 24.4.

After the crystals had been removed, the ether was driven out of the ether solution, and the excess of unreacted 1-diethylamino-4-aminopentane was driven off in vacuo. The residue was an oil, which decomposed when distilled in vacuo (3 mm), giving off α-aminopyridine. The presence of the latter was demonstrated by the mixed melting point of the decomposition product and α-aminopyridine (mixed melting point 92°) and by preparing the picrate with a m.p. of 210° (picrate of α-aminopyridine). We managed to isolate a crystalline part of the synthesized base from the oily product as the dipicrate, m.p. 179-180°. This was prepared by driving the excess 1-diethylamino-4-aminopentane out of 1.2 g of the reaction mixture and then dissolving the residue in anhydrous ethyl acetate, adding 1.7 g of picric acid dissolved in ethyl acetate. The mixture warmed up noticeably as the two solutionswere poured together, an oil settling out at once and soon crystallizing. This yielded 2.6 g of the dipicrate, m.p. 167-170°. The m.p. rose to 179-180° after two recrystallizations from methanol.

Analysis of the dipicrate of (I): 4.067 mg substance: 7.068 mg CO_2; 1.684 mg H_2O. 4.120 mg substance: 7.127 mg CO_2, 1.630 mg H_2O. 2.443 mg substance: 0.395 ml N_2 (17°, 737 mm). 2.166 mg substance: 0.393 ml N_2 (19°, 739.5 mm). Found %: C 47.43, 47.18; H 4.63, 4.43; N 20.85, 20.85. $C_{32}H_{36}O_{14}N_{12}$. Calculated %: C 47.29; H 4.43; N 20.69.

The base was recovered as an oil from this dipicrate. When the oil was saponified with dilute sulfuric acid, carbon dioxide was evolved (absorbed in baryta water), and α-aminopyridine and 1-diethylamino-4-aminopentane were recovered.

In addition to the dipicrate, we isolated the oxalate, m.p. 170-171°. The hydrochloride, the sulfate, the tartrate, and some other salts were isolated as non-crystallizing oils.

Sym-di-2-pyridyl-(3'-diethylaminopropyl)-guanidine (II). We prepared 1-diethylamino-3-aminopropane by the method described by Terentyev and Kost [9] for use in synthesizing this derivative. 4.6 g of dipyridylthiourea, 3.5 g of 1-diethylamino-3-aminopropane, 40 g of basic lead carbonate, and 50 ml of absolute alcohol were heated as specified above to 70-75° for 5 hours. The dipicrate, m.p. 176-181°, was isolated. The m.p. of the dipicrate rose to 187° after double recrystallization from methanol.

Analysis of the dipicrate of (II): 3.723 mg substance: 6.266 mg CO_2, 1.400 mg H_2O. 3.581 mg substance: 6.045 mg CO_2, 1.331 mg H_2O. 2.384 mg substance: 0.453 ml N_2 (16.5°, 738 mm). 2.343 mg substance: 0.444 ml N_2 (17.5°, 737.5 mm). Found %: C 45.93, 46.07, H 4.21, 4.16; N 21.76, 21.61. $C_{30}H_{32}O_{14}N_{12}$. Calculated %: C 45.91; H 4.08; N 21.42.

The m.p. of the oxalate was 167-170°.

None of the crystalline by-product observed in the synthesis of (I) was found in this case.

Sym-di-2-pyridyl-(4'-diethylaminobutyl)-guanidine (III). 1,4-diethylaminobutylamine was prepared by the Strukov method [10]. 4.5 g of dipyridylthiourea was dissolved in 50 ml of absolute alcohol, and 5 g of 1,4-diethylaminobutylamine and 40 g of pulverized lead carbonate were added. The mixture was heated, with stirring, to 70° for 7 hours, after which the precipitate was filtered out, and the alcohol was driven out of the filtrate, followed by the unreacted amine (in vacuo). When the alcohol was driven off, a crystalline precipitate settled out, which was filtered and washed with ether. This yielded 0.4 g of the crystalline precipitate, which had a m.p. of 226-227° after recrystallization from water.

Analysis of the crystalline precipitate: 3.350 mg substance: 7.080 mg CO_2; 1.055 mg H_2O; 1.319 mg SO_4. 3.280 mg substance: 6.912 mg CO_2; 1.022 mg H_2O: 1.347 mg SO_4. 3.927 mg substance: 0.835 ml N_2 (18°, 742.5mm). Found %: C 57.67, 57.51, H 3.52, 3.49; N 24.37; S 13.14, 13.70.

After the crystalline precipitate had been filtered out, the ether was driven out of the ether solution of the principal reaction product, and the residual oil was dried in vacuo after the excess 1,4-diethylaminobutylamine had been driven off. The dipicrate was prepared by dissolving 0.7 g of the resultant oil in ethyl acetate and adding a solution of 1 2 g of picric acid in ethyl acetate An oil separated out at once, crystallizing completely. This yielded 1.3 g of the dipicrate, m.p. 155-158°. Double recrystallization from methanol yielded 0.5g with a m.p. of 170-171°.

Analysis of the dipicrate of (III):3.889 mg substance: 6.685 mg CO_2; 1.512 mg H_2O. 3 406 mg substance: 5 805 mg CO_2; 1.334 mg H_2O. 4.00 mg substance: 6.880 mg CO_2; 1.600 mg H_2O. 6.1479 mg substance: 1.16 ml N_2 (19°, 734 mm). 5.2875 mg substance: 1 01 ml N_2 (20°, 735 mm). Found %: C 46.91, 46.51, 46.94; H 4.37, 4.38, 4.47, N 20.88, 21.11. $C_{31}H_{34}O_{14}N_{12}$. Calculated %: C 46.61; H 4.26; N 21.05.

The m.p. of the oxalate was 191-194°.

Sym-di-(5-chloropyridyl)-thiourea (IV). Sym-di-(5-chloropyridyl)-thiourea was synthesized from β'-chloro-α-aminopyridine and carbon disulfide. The β'-chloro-α-aminopyridine was prepared by chlorinating α-aminopyridine by the Chichibabin and Egorov method [11]. 20 g of β'-chloro-α-aminopyridine, m.p. 130-133°, 40 ml of carbon disulfide, 0.2 g of sulfur, and 50 ml of absolute alcohol were refluxed on a water bath for 50 hours. The excess carbon disulfide and alcohol were driven off on a water bath. The unreacted β'-chloro-α-aminopyridine was eliminated from the resulting sym-di-(5-chloropyridyl)-thiourea by recrystallizing the latter from butyl alcohol. This yielded 6 g of sym-di-(5-chloropyridyl)-thiourea, m.p. 214-216°, 11.5 g of β'-chloro-α-aminopyridine (m.p 123-125°) being recovered. The yield of sym-di-(5-chloropyridyl)-thiourea was 55%, based on the reacted β'-chloro-α-aminopyridine. After double recrystallization from isobutyl alcohol the sym-di-(5-chloropyridyl)-thiourea had a m.p. of 214-216°.

3.105 mg substance. 5 013 mg CO_2; 0.806 mg H_2O. 3.187 mg substance: 5.151 mg CO_2; 0.812 mg H_2O. 2 255 mg substance: 0.369 ml N_2 (17.5°, 750 mm). 5.2213 mg substance: 0.880 ml N_2 (22°, 748 mm). Found %: C 44.06 44.11; H 2.90,2.84; N 18.54, 18.74. $C_{11}H_8N_4Cl_2S$. Calculated %: C 44.15; H 2.67; N 18.73.

Sym-di-2-(5-chloropyridyl)-(4'-diethylamino-1'-methylbutyl)-guanidine (V). 3 g of sym-di-(5-chloropyridyl)-thiourea was heated in 150 ml of butyl alcohol to which 6 g of 1-diethylamino-4-aminopentane had been added until it dissolved. After the thiourea had dissolved, 40 g of finely pulverized basic lead carbonate was added with constant mechanical stirring, and heating was continued for 5 hours at 110°. After filtering while hot, the precipitate was washed with hot butyl alcohol.

The butyl alcohol was distilled from the filtrate in vacuo until the latter had been reduced to a volume of 5 ml, a precipitate being thrown down. The precipitate was filtered out and washed with absolute ether. This yielded 0.3 g of a substance which did not fuse below 270° and contained sulfur. After the precipitate had been filtered out of the ether solution, the ether was driven off, and the excess 1-diethylamino-4-aminopentane was driven off in a 3-mm vacuum. The residue did not distil; it was a thick brown oil. The dipicrate of (V) was prepared by dissolving 0.9 g of the residual oil in anhydrous ethyl acetate (after the excess 1-diethylamino-4-aminopentane had been driven off), and a solution of 1.2 g of picric acid in ethyl acetate was added. When the solutions were poured together,

an oil that crystallized settled out. This yielded 1.1 g of the dipicrate, m.p. 157-163° first recrystallization from butyl alcohol yielded 0.4 g with a m p of 169-170°, a second recrystallization yielding 0.3 g with a m p of 169-170° This dipicrate was also prepared by another method: 2 g of the reaction mixture was dissolved in 10 ml of isobutyl alcohol and heated, after which a solution of 2.5g of picric acid in 10 ml of isobutyl alcohol was added. When the two solutions were combined, an oil, part of which crystallized, settled out Adding a small amount of acetone (about 5 ml) dissolved the uncrystallized oil, the crystalline picrate setting out. The picrate was filtered out and washed again with acetone. This yielded 2.5 g of the dipicrate, m.p. 169-171°.

Analysis of the dipicrate of (V): 3.317 mg substance: 5.303 mg CO_2; 1.197 mg H_2O. 3.314 mg substance: 5.304 mg CO_2; 1.204 mg H_2O. 2.200 mg substance: 0.366 ml N_2 (19°, 752 mm). 2.253 mg substance: 0.370 ml N_2 (18°, 752 mm). 3.780 mg substance: 0.637 ml N_2 (20°, 741 mm). Found %: C 43.71, 43.68; H 4.04, 4.06; N 19.24, 19.06, 19.14. $C_{32}H_{34}O_{14}N_{12}Cl_2$. Calculated %: C 43.59; H 3.86; N 19.07.

Sym-di-2-(5-chloropyridyl)-(3-diethylaminopropyl)-guanidine (VI) 2.3 g of di-(5-chloropyridyl)-thiourea, 2 g of 1-diethylamino-3-aminopropane, 150 ml of butyl alcohol, and 40 g of basic lead carbonate were heated as described previously for 5 hours at 105-110°. The dipicrate was prepared from the residue left after filtering out the precipitate, driving off the butyl alcohol, and driving off the excess 1-diethylamino-3-aminopyridine in vacuo. 1 g of the reaction mass yielded 1 g of the dipicrate, m.p. 183-186°, which was raised to 185-186° after recrystallization from butyl alcohol, and remained at 185-186° after a second recrystallization.

Analysis of the dipicrate of (VI): 2.843 mg substance: 4.426 mg CO_2; 0.902 mg H_2O. 2.880 mg substance: 4.489 mg CO_2; 0.900 mg H_2O. 2.472 mg substance: 0.425 ml N_2 (21°, 747 mm). 4.1616 mg substance: 0.735 ml N_2 (22°, 747 mm). Found %: C 42.49, 42.54; H 3.54, 3.50; N 19.62, 19.67. $C_{30}H_{30}O_{14}N_{12}Cl_2$. Calculated %: C 42.2; H 3.52; N 19.69.

SUMMARY

1. The reaction of sym-dipyridylthiourea with aliphatic amines in the presence of a desulfurizing agent has yielded new dialkylamino alkyl substitution drivatives of sym-dipyridylguanidine.

2. The action of carbon disulfide upon 5-chloro-2-aminopyridine has yielded the new sym-di-(5-chloropyridyl)-thiourea, from which the respective substitution drivatives of chloropyridylguanidine have been synthesized by the method set forth in Par.1.

3. The compounds (I), (II), and (V) proved to be inactive in bird malaria.

4. In the reactions described in Par.1, a by-product with a m.p. of 227° was secured, which according to its percentages of carbon, hydrogen, nitrogen, and sulfur, is dipyridylthiourea, the two known forms of which fuse at 147° and 163°. In contrast to the latter compounds, the substance with a m.p. of 227° does not form guanidines.

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Received November 14, 1949.

1,2-NAPHTHO-(3',4')-FURAZAN-3- AND 4-SULFONIC ACIDS

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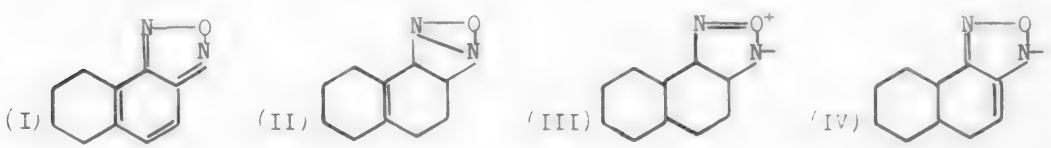
1,2-Naphtho-(3',4')-furazan was synthesized for the first time by Goldschmidt [1] by dehydrating 1,2-naphthoquinonedioxime. The method of synthesis led the author to adopt the formula of an anhydride of the dioxime [I] for the compound. Green and Rowe [2] rejected this quinoid structure and proposed the formula (II) on the basis of the absence of color in furazan compounds and their high resistance to oxidizing and reducing agents. Later, Hammick and his co-workers [3] stated that benzofurazan added 4 atoms of bromine, and again adopted the quinoid structure for compounds of this sort Ya.Syrkin and E.Shott-Lvova [4] concluded from measurements of the dipole moment of naphthofurazan that it could have the structure of (III), in which the structure of the naphthalene ring was retained, or of (IV).



Not much research has been done on the chemical properties of naphthofurazan and only a limited number of its derivatives are known. Naphthofurazan-3-carboxylic acid [5] and naphthofurazan-6- and 7-sulfonic acids [6] have been synthesized indirectly, i.e., via the respective substitution derivatives of 1-nitroso-2-naphthol. Direct nitration of naphthofurazan results in formation of two mononitro compounds and one dinitro compound, depending upon the conditions [7]; the structure of these compounds has not been established. In one of the mononitro compounds the nitro group is in either the 3 or 4 position, and in the 5 or 8 position in the other. Both of the mononitro compounds yield the same dinitro compound upon further nitration.

It is stated in the literature that naphthofurazan dissolves in concentrated sulfuric acid without change. Our observations have shown that this is true only at room temperature, the naphthofurazan being sulfonated at higher temperatures. When 1 part of naphthofurazan is heated with 0.8 part of concentrated sulfuric acid to 160° for 4 hours, for example, most of the naphthofurazan is converted into a sulfo acid. Sulfonation takes place even at room temperature when oleum is added to a sulfuric acid solution of naphthofurazan, 70% of the naphthofurazan used settling out as the sodium salt of the sulfo acid when the sulfonated mass is partially neutralized with soda. Oxidation of the precipitated sulfo acid with chromic acid yields phthalic acid. It follows, therefore, that the sulfo group is located in that part of the naphthalene ring that is linked to the furazan ring, i.e., in the 3 or 4 position. Naphthofurazan-4-sulfonic acid was synthesized to determine the position of the sulfo group. The composition of its sodium and barium salts, as well as the melting point of its sulfochloride and the ease with which it could be hydrolyzed,

proved that it was different from the sulfonation product. Whereas the sulfonation product loses a sulfo group when it is boiled with 66-70% sulfuric acid, naphthofurazan-4-sulfonic acid remains unchanged when so treated. Hence, the sulfo acid synthesized by direct sulfonation is naphthofurazan-3-sulfonic acid. This sort of sulfonation agrees best with the formulas (IV) and (III) for naphthofurazan proposed by Ya.Syrkin and E.Shott-Lvova. In this connection it is worthy of note that 2-phenyl-1',2'-naphtho-1,2,3-triazole, whose structure is like that of 1,2-naphtho-(3' 4')-furazan, is also sulfonated at the 3' position [8]. The method we employed to secure naphthofurazan-3-sulfonic acid did not guarantee, of course, that none of the possible isomeric monosulfo acids and products of more far reaching sulfonation would not be lost.

We prepared naphthofurazan-4-sulfonic acid by reacting 1-nitroso-2-naphthol-4-sulfonic acid with hydroxylamine hydrochloride in the presence of sodium acetate or sodium hydroxide, and dehydrating the resultant 1,2-naphthoquinonedioxime-4-sulfonic acid by heating it in an alkaline medium. If substances that neutralize the liberated hydrochloric acid are not employed in the reaction with hydroxylamine hydrochloride, at a temperature as low as 15–20°, the resultant dioxime loses the oxime group at the 1 position and is converted into 2-nitroso-1-naphthol-4-sulfonic acid. Analogous hydrolysis of the oxime group has previously been observed in the case of 1,2-naphthoquinonedioxime-6-and 7-sulfonic acids, but under more severe conditions [9].

EXPERIMENTAL

(Together with A.G.Studensky)

Sulfonation of naphthofurazan. 50 ml of 56% oleum was added during the course of one and a half hours at 20° to a solution of 11.8 g of naphthofurazan in 70 ml of 98% sulfuric acid, and the mixture was kept at 20° for 4 hours. The sulfo mass was dissolved in ten times its weight of water, and 18 g of soda was added, the precipitate being filtered 5 hours later and washed with water and alcohol. The yield was 14.5 g. The filtrate was neutralized with chalk, the gypsum filtered out, and the filtrate partially evaporated, yielding 1.1 g of the substance. The overall yield of the sodium salt of the sulfo acid was 75% of the theoretical. The sodium salt crystallized from aqueous alcohol as colorless needles, which were water-soluble but insoluble in alcohol.

0.7761 g substance: losses in drying (140°) 0.0697 g. 0.2372 g substance: 0.0557 g Na_2SO_4. 0.3451 g dry substance: 0.0884 g Na_2SO_4. Found %: H_2O 8.98; Na 7.61, 8.30. $C_{10}H_5O_4N_2SNa \cdot 1.5\ H_2O$. Calculated %: H_2O 9.03; Na 7.69. $C_{10}H_5O_4N_2SNa$. Calculated %: Na 8.45.

Barium salt. Platelets, slightly soluble in hot water.

0.8250 g substance: losses in drying (180°) 0.0445 g. 0.6451 g, dry substance: 0.2413 g $BaSO_4$. Found %: H_2O 5.39; Ba 22.01. $(C_{10}H_5O_4N_2S)_2\ Ba \cdot 2H_2O$. Calculated %: H_2O 5.36. $(C_{10}H_5O_4N_2S)_2\ Ba$. Calculated %: Ba 21.62.

Sulfochloride. Rhombic platelets (from benzene), m.p. 171°.

Hydrolysis of the sulfo acid. A solution of 2.5 g of the sodium salt of the sulfo acid in 50 ml of 66-70% sulfuric acid was refluxed for 10 hours. The resulting naphthofurazan was extracted with ether and the ether solution was evaporated. The yield of naphthofurazan (m.p. 78°) was 56-59% of the theoretical. When 50% sulfuric acid was used, only traces of naphthofurazan were obtained. The hydrolysis of the sulfochloride followed the same pattern.

Oxidation of the sulfo acid. 5 g of pulverized potassium dichromate was added in two batches to a boiling solution of 1.5 g of the sodium salt in 15 ml of 95% acetic acid. After the mixture had been boiled for 20 hours, it was diluted with 50 ml of water, and the precipitate was filtered out. The substance crystallized from alcohol as colorless platelets with a m.p. of 195°, which contained neither nitrogen nor sulfur, exhibited a positive reaction for phthalic acid with resorcinol, and sublimed to yield needles of phthalic anhydride, m.p. 128°.

Reactions of 1-nitroso-2-naphthol-4-sulfonic acid with hydroxylamine. a) Alkaline medium. A solution of 2 g of sodium hydroxide in 20 ml of water was added to a suspension of 6.2 g (0.02 mol) of the sodium salt of nitrosonaphtholsulfonic acid in 20 ml of water, and then 2.8 g (0.04 mol) of hydroxylamine hydrochloride was added. The mixture was stirred for an hour at room temperature and then boiled for 5 minutes. The resultant precipitate (needles with sheared-off ends) was filtered after it had cooled and then washed with water and alcohol, the yield being 2.5 g. The substance crystallized from aqueous alcohol as nearly colorless stubby needles, which were rather freely soluble in water.

b) In the presence of sodium acetate. 1.4 g of hydroxylamine hydrochloride was added to a solution of 3.1 g of the sodium salt of the nitroso compound and 3.2 g of crystalline sodium acetate in 20 ml of water, and the mixture was allowed to stand for an hour at room temperature. The slight orange precipitate was filtered out, and the solution was alkalinized with 5 ml of 40% sodium hydroxide and heated to a boil. The resultant precipitate was filtered out and washed, the yield totaling 0.7 g. After the substance had been crystallized from aqueous alcohol, it had the same appearance and properties as that secured earlier.

A mixture of the substances prepared by methods a) and b) was analyzed and converted into the sulfochloride. The substance displayed no losses in weight when heated to 140°.

0.1958 g, 0.1699 g substance: 0.0482 g, 0.0418 g Na_2SO_4. Found %: Na 7.97, 7.97. $C_{10}H_5O_4N_2SNa \cdot H_2O$ Calculated %: Na 7.93.

The barium salt was slightly soluble in cold water and readily soluble in hot water; it crystallized from water as needles with sawed-off ends. Heating it to 140° caused no loss of weight.

0.1648 g substance: 0.0597 g $BaSO_4$. Found %: Ba 21.32. $(C_{10}H_5O_4N_2S)_2Ba$. Calculated %: Ba 21.62.

The sulfochloride had a m.p. of 113-113.5° after recrystallization from benzene. Boiling the sodium salt of the sulfo acid and the sulfochloride with 70% sulfuric acid did not split out the sulfo group.

c) With no neutralizing agents present. 1.4 g of hydroxylamine hydrochloride was added to a solution of 3.1 g of the sodium salt of the nitroso compound in 20 ml of water, and the solution was stirred for half an hour at room temperature. The resulting precipitate was filtered out and washed with alcohol, the yield totaling 1.1 g of water-soluble yellow needles. Its solutions were colored an intense green-yellow by ferrous salts, indicating the presence of o-nitrosonaphtholsulfonic acid, though they formed no precipitate with aniline water, which was evidence that the initial 1-nitroso-2-naphthol-4-sulfonic acid was absent [10]. When the substance was reduced with stannous chloride, it was converted into 2-amino-1-naphthol-4-sulfonic acid, while heating it with 10% nitric acid converted it into 2,4-dinitro-1-naphthol, thus proving that it was 2-nitroso-1-naphthol-4-sulfonic acid.

SUMMARY

1. 1,2-Naphtho-(3',4')-furazan-3-sulfonic acid is the principal product of the reaction of 1,2-naphtho-(3',4')-furazan with fuming sulfuric acid at room temperature.

2. The direction taken by the reaction of 1-nitroso-2-naphthol-4-sulfonic acid with hydroxylamine depends upon the conditions employed: the action of hydroxylamine hydrochloride yields 2-nitroso-1-naphthol-4-sulfonic acid, neutralization of the hydrochloric acid liberated, followed by heating in an alkaline medium, yielding 1,2-naphtho-(3',4')-furazan-4-sulfonic acid.

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Received December 28, 1949.

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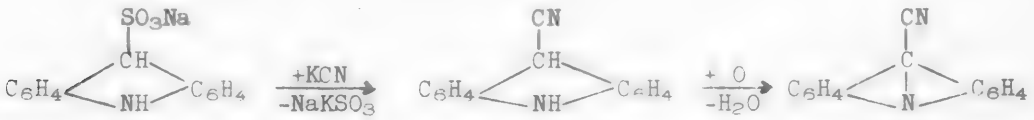
MESO DERIVATIVES OF ACRIDINE

XXII. 9-CYANACRIDINES AND THEIR SYNTHESIS FROM ACRIDINES

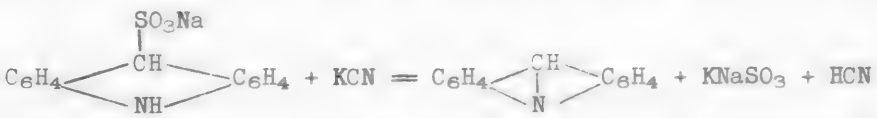
N S. Drozdov and O. M. Cherntsov

In one of our preceding papers [1] we described a general method of synthesizing 9-cyanacridines by reacting 9-methoxy-9-hydroxy-9, 10-dihydroacridines (9-methoxy-9-hydroxyacridans) with hydrocyanic acid. We now have made a more detailed study of the formation of 9-cyanacridines by reacting hydrocyanic acid with acridines and by reacting potassium cyanide with the products of the addition of bisulfite to the acridines described in our preceding paper [2]. We tried to secure experimental data describing the reaction in which 9-cyanacridines are formed and the properties of the above-mentioned compounds of bisulfite and the acridines, inasmuch as the problem of the structure of these compounds had been touched on by us in our previous paper.

K. Lehmstedt and E. Wirth [3] prepared 9-cyanacridine by heating an aqueous-alcoholic solution of potassium cyanide with an aqueous-alcoholic solution of the product of the reaction between acridine and sodium bisulfite to which they assigned the structure of the sodium salt of 9,10-dihydroacridine-9-sulfonic acid (acridan-9- sulfonic acid). These authors found that the immediate product of the reaction of the sodium salt of acridan-9-sulfonic acid with cyanide was 9,10-dihydro-9-cyanacridine (9-cyanacridan), which is readily oxidized to 9-cyanacridine by mere exposure to the air. They therefore believed that 9-cyanacridine was formed as follows:



Small amount of 9,10,9',10'-tetrahydro-9,9'-biacridyl were formed as a by-product in this reaction. In a later paper [5] Lehmstedt found that 9,10-dihydro-9-cyanacridine is formed as the principal reaction product when acridine hydrochloride and potassium cyanide or free acridine and hydrocyanic acid are heated for a short time in an aqueous-alcoholic solution. In benzene, on the other hand, this latter reaction resulted in the formation, principally, of 9,10,9',10'-tetrahydro-9,9'-biacridyl. Lehmstedt regarded these observations of his as proof that the first stage of the reaction between a salt of acridan-9-sulfonic acid and cyanide was the formation of free acridine and hydrocyanic acid.

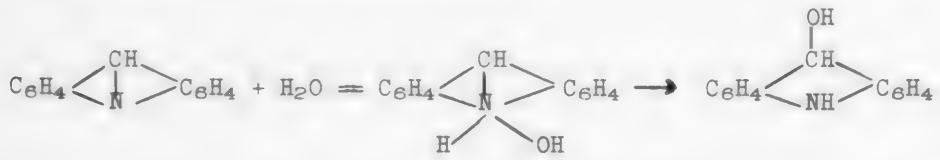


their further interaction resulting in the formation of 9-cyanacridan (9,10-dihydro-9-cyanacridine).

Our experiments have shown that when the simplest sodiumacridinium sulfite ("the sodium salt of acridan-9-sulfonic acid") or the respective derivatives of 2-methyl- and 2-methoxyacridines are heated in an aqueous-alcoholic solution, the principal reaction products are the 9-cyanacridines. High yields are secured only in the first case, the yields in the last two being much lower. We did not isolate 9-cyanacridans as intermediate products, probably owing to their rapid oxidation to 9-cyanacridines during the recovery and refining of the reaction products. Microscopic examination of the crystalline structure of the crude reaction products, however, indicated that they differed from the 9-cyanacridines secured after further refining. The isolated 9-cyanacridines were identical with the compounds that we had previously prepared by another method [1]. They are well-crystallizable substances that are fairly freely soluble in acetic acid, hot alcohol, benzene, and chloroform, and only slightly soluble in ether and petroleum ether. When heated in dilute mineral acids, they dissolve, thus displaying weak basic properties. As nitriles, the 9-cyanacridines are rather stable.

Our other experiments aimed at securing direct proof that the only role of the sulfite radical in all the instances mentioned above is to drive hydrocyanic acid out of the cyanide, the acid then reacting with the acridans to form 9-cyanacridans or the respective 9-cyanacridines. This was done by heating the acridines with an equivalent quantity of bisulfite or bicarbonate and potassium cyanide in an aqueous-alcoholic medium, a yield of 45-60% of the theoretical of the respective 9-cyanacridines being recovered from the reaction mixture together with the unreacted acridine. The results of these experiments thus demonstrate that the 9-cyanacridines are actually produced in the reaction of sodiumacridinium sulfites with potassium cyanide as the result of the interaction between the acridines and the hydrocyanic acid.

The nature of this interaction may be elucidated if we bear in mind the differences in the course of the reaction between the acridines and hydrocyanic acid that are due to the properties of the reaction medium. Whereas this interaction results in the formation of 9-cyanacridans (or the corresponding 9-cyanacridines) in an aqueous-alcoholic medium, the yield of 9-cyanacridines is negligible in an anhydrous medium, say, in benzene, the principal reaction product being 9,10,9',10'-tetrahydro-9,9'-biacrydyl, as Lehmstedt proved in his research. These findings, which are evidence of the influence of water upon the reaction between the acridines and hydrocyanic acid, compel us to assume that the latter does not react with free acridines, but rather with the pseudobases formed by isomerization of the true acridinium bases, which originate, in turn, when water is added to acridans:

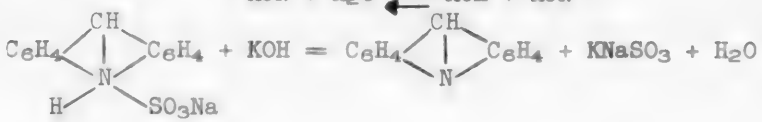


The results we secured in our earlier study of the reaction between the pseudohydrates of 9-methoxyacridines and hydrocyanic acid [1] are another indirect confirmation of this concept of the nature of the interaction of hydrocyanic acid and the acridines.

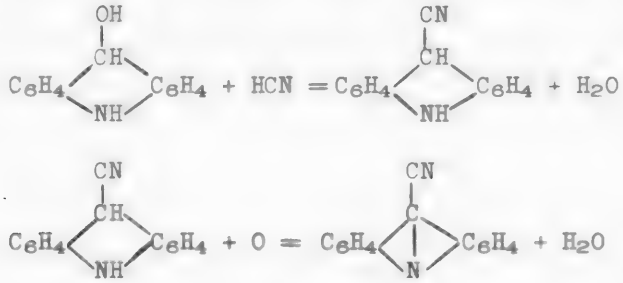
Hence the results of our experiments in the reaction of sodiumacridinium sulfites with potassium cyanide are not only further evidence in support of the concept we adopted in our preceding paper [2] regarding the structure of the

products of the reaction of the acridines with bisulfite, but also enable us to explain the reaction sequence in the formation of the 9-acridines from these compounds. In a medium that contains water, the action of the alkali produced by hydrolysis of the cyanide rapidly decomposes the sodiumacridinium sulfite into acridine and a mineral sulfite:

$$KCN + H_2O \rightleftharpoons KOH + HCN$$



Then the addition of water to the acridine results in the formation of a pseudo-base, which reacts with the hydrocyanic acid; splitting out the water yields 9-cyanacridan (9,10-dihydro-9-cyanacridine), which is then oxidized to 9-cyanacridine.



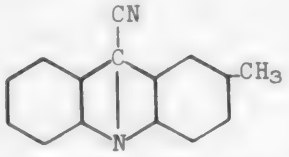
EXPERIMENTAL

9-Cyanacridine. 10 g of sodiumacridinium sulfite was suspended in 50 ml of alcohol and heated to a gentle boil, a solution of 2.5 g of potassium cyanide in 7-8 ml of water being added to the boiling suspension. The mixture was heated for 40 minutes and agitated after which the solvent was driven off and the solid residue triturated in a mortar with a 5% solution of sodium hydroxide. The washed residue was set aside to stand overnight exposed to the air and then dissolved in benzene, the minute quantity of insoluble impurities (9,10,9' 10'-tetrahydro-9,9'-biacridyl, m.p. 214°) being filtered out of the solution, and the filtrate shaken for about one hour with a 10% solution of sodium bisulfite to eliminate the acridine it contained. The benzene layer was separated from the bisulfite extract (alkalinization of which regenerated a small quantity of acridine), and the greenish impurities that settled out upon standing were filtered out, after which the benzene was driven off to dryness. The not wholly pure 9-cyanacridine left after the distillation was recrystallized from boiling ethyl alcohol to which activated charcoal had been added. The 9-cyanacridine was secured as silky, lemon-yellow needles, m.p. 180-181°. The yield of the pure substance was 5.1-5.5 g, or 80-85% of the theoretical.

The same substance was synthesized by reacting acridine with hydrocyanic acid. 0.9 g of acridine was dissolved in 30 ml of ethyl alcohol, 0.6 g of sodium bicarbonate and a solution of 0.5 g of potassium cyanide in 3 ml of water were added, and the resultant mixture was refluxed for 2 hours. The reaction product, recovered by diluting the solution with 2 or 3 times its volume of water or by driving off the solvent was refined by the procedure outlined above. The yield of pure 9-cyanacridine, m.p. 180.5-181°, averaged 0.6 g, or about 60% of the theoretical.

The identity of the two substances prepared by the methods described was established by means of a mixed fusion test. On the other hand, all the properties of these substances are the same as those of the 9-cyanacridine prepared previously from 9-methoxy-9-hydroxy-9,10-dihydroacridine or from 9,9'-diphenoxyacridine hydrochloride [1].

2-Methyl-9-cyanacridine



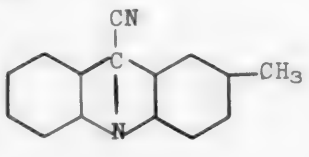
50 ml of alcohol was added to the sodium-2-methylacridinium sulfite prepared from 1.9 g of 2-methylacridine by the method described in our preceding paper, and the resulting suspension was heated to boiling. While the boiling solution was agitated, a solution of 0.7 g of potassium cyanide in 5 ml of water was added, and the boiling and stirring were continued for another 30-40 minutes. The alcohol was driven off, and the solid residue was extracted with water to eliminate the mineral salts and then triturated in a mortar with a 5% solution of sodium hydroxide, washed on a filter with water, and exposed to the air overnight. The residue was extracted with benzene, the insoluble impurities being eliminated by filtration, and the benzene extract was agitated for 30 minutes with a 10% solution of bisulfite to eliminate the unreacted 2-methyl-acridine. The benzene extract was separated from the aqueous layer, allowed to stand for 2 hours, and then filtered. The filtrate was evaporated to dryness and the residue was recrystallized from hot alcohol containing activated charcoal. The 2-methyl-9-cyanacridine was secured as golden-yellow needles, m.p. 178.5-179°.

0.1507 g subs.: 17.0 ml N_2 (15°, 750 mm). Found %: N 12.98.
$C_{15}H_{10}N_2$. Calc. %: N 12.85.

The yield of the 2-methyl-9-cyanacridine totaled 1.0 g, or 44-46% of the theoretical (based on the 2-methylacridine used). About 0.8 g of 2-methylacridine was recovered from the bisulfite extract and the sodium-2-methylacridinium sulfite mother liquor.

2-Methyl-9-cyanacridine is produced by reacting 2-methylacridine with hydrocyanic acid directly. 0.95 g of 2-methylacridine was dissolved in 30 ml of ethyl alcohol, 0 6 g of sodium bicarbonate and a solution of 0.5 g of potassium cyanide in 3 ml of water were added, and the mixture was refluxed for 2 hours. The reaction product was isolated and refined as in the previous experiments about 0 3 g of 2-methylacridine being recovered. The 2-methyl-9-cyanacridine that was separated from the latter was recrystallized from hot alcohol, yielding 0.5 g of the crystalline substance with a m.p. of 178-179°. The yield of the pure 2-methyl-9-cyanacridine was 48% of the theoretical, based on the 2-methylacridine used. The synthesized 2-methyl-9-cyanacridine was identical with that prepared by the method described above and with that prepared from 2-methyl-9-methoxy-6-hydroxyacridan [1].

2-Methoxy-9-cyanacridine



A suspension of 4.8 g of sodium-2-methoxyacridinium sulfite in 30 ml of alcohol was heated to boiling, and a solution of 0.7 g of potassium cyanide in 3 ml of water was added. The mixture was heated and stirred for 1.5 hours. The reaction product was isolated and refined as described in the analogous experiments above. The synthesized substance was finally refined by dissolving it in a small amount of alcohol, the solution being boiled with activated charcoal and diluted while hot with about twice its volume of water. The 2-methoxy-9-cyanacridine crystallized as small lemon-yellow needles, m.p. 185°.

0.1378 g subs.: 14.5 ml N_2 (17°, 762 mm). Found %: N 12.19.
$C_{15}H_{10}ON_2$. Calc. %: N 11.97.

The yield of the 2-methoxy-9-cyanacridine totaled 1.3 g, or 55% of the theoretical. It was identical with the 2-methoxy-9-cyanacridine prepared from 2,9-dimethoxy-9-hydroxyacridan [1].

2-Methoxy-9-cyanacridine is produced by reacting 2-methoxyacridine with hydrocyanic acid. 0.6 g of sodium bicarbonate and a solution of 0.5 g of potassium cyanide in 3 ml of water were added to 1 g of 2-methoxyacridine in 30 ml of ethyl alcohol, and the mixture was heated to boiling for 2 hours. The reaction product was isolated and refined as outlined above. The synthesized substance had a m.p. of 185° and possessed all the properties of 2-methoxy-9-cyanacridine. The yield averaged 0.5 g (45% of the theoretical).

SUMMARY

It has been found that 9-cyanacridines are the principal reaction products when sodiumacridinium sulfite and the corresponding derivatives of 2-methyl- and 2-methoxy-acridines are reacted with potassium cyanide in an aqueous-alcoholic medium. The same 9-cyanacridines are synthesized by heating the acridines in an aqueous-alcoholic medium with the calculated quantity of the bisulfite or bicarbonate and potassium cyanide.

The formation of the 9-cyanacridines when sodium-acridinium sulfites are reacted with potassium cyanide in a medium containing water is the result of several successive reactions, the first of which being decomposition of the sodiumacridiniums by the alkali formed by hydrolysis of the cyanide, yielding acridines.

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[1]) See Consultants Bureau English translation, p. 1885.

EDITORIAL NOTE

The following corrections must be made in the literature references to the paper by R.A.Konovalova, B.S. Diskina, and M.S.Rabinovich, "Alkaloids of some species of the legume family. X. New alkaloids from Piptanthus nanus." M. Pop. Piptanthin and piptamin," printed in J. Gen. Chem., 21, 773 (1951):

No.	Reads	Should read
	Page 773,[1] Table 1, Column 6	
4	A.P.Orekhov, E.L.Gurevich [5] [6]	A.P. Orekhov, S.S.Norkina, and E.I. Gurevich [5] [6]
6	A.P Orekhov [9]	A.P.Orekhov and S.S.Norkina [9]
7	A.P Orekhov [10]	S.S. Norkina and A.P.Orekhov [10]
8	A.P Orekhov and T. Narkuziev [11]	S S.Norkina, T. Narkuziev, and A. P. Orekhov [11]

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[5] A.P. Orekhov, E. Gurevich, Ber., 66, 625 (1933).	[5] A.P. Orekhov, S.S. Norkina, E.L. Gurevich, Ber., 66, 625 (1933).
[6] A.P. Orekhov, E. Gurevich, Ber., 67, 1394 (1934)	[6] A P. Orekhov, S.S. Norkina, E.L. Gurevich, Ber., 67, 1394 (1934).
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[1] See Consultants Bureau English translation, p. 853.

[2] See Consultants Bureau English translation, p. 860.

TABLE

Diffusion Currents and the Concentrations Calculated from These Currents

Substance	Benzoic acid			Salicylic acid			Oxalic acid			Malonic acid			Lactic acid							Glycolic acid					
c, mmol/liter, actual concentration.....	3.09	5.5	7.91	10.7	2.0	3.92	6.3	7.73	1.0	2.0	4.0	3.0	3.5	5.0	7.31	8.0	3	4	5	6	7	1	2	3	4	5	6
id, microamperes, exptl.....	5.1	10.2	16.1	18.8	4.6	9.0	14.6	20.2	3.76	7.75	12.79	17.12	7.3	7.75	13.4	16.92	18.1	4.6	6.7	9.3	12.3	15.2	2.8	6.65	8.8	12.2	15.0	17.6
$\frac{id}{c}$ (mean)																												
κ A·l/mmol...			1.87			2.38			4.13						2.42					1.86					2.99		
c mmol/l, conc. as calculated from the id....	2.8	5.6	8.8	10.3	1.94	3.8	6.16	8.5	0.93	1.92	3.16	4.23	3.07	3.25	5.62	7.11	7.6	2.46	3.6	5.0	6.6	8.2	0.94	2.2	2.9	4.1	5.0	5.9

Fig. 1. Apparatus for catalytic cracking in the presence of boron fluoride.
1) Cracking column; 2) receiver; 3) electric heating coil; 4) catalyst zone; 5) evaporating section; 6) thermocouple pocket; 7) flask for generating BF_3; 8) oil bath; 9) buret for etherate supply; 10) condenser; 11) bubble counter; 12) raw material buret; 13) full cylinder; 14) raw material collector; 15) drop counter; 16) condenser; 17 BF_3 absorbers; 18) manometer; 19) gasometer; 20) filling funnel for buret; 21) mercury thermometer; 22) thermocouple; 23) Dewar flask; 24) cold junction of thermocouple; 25) millivoltmeter. B - Alternative supply system